SCIENCE
UNIVERSITY OF COPENHAGEN

Electron-vibron coupling in single-molecule transistors

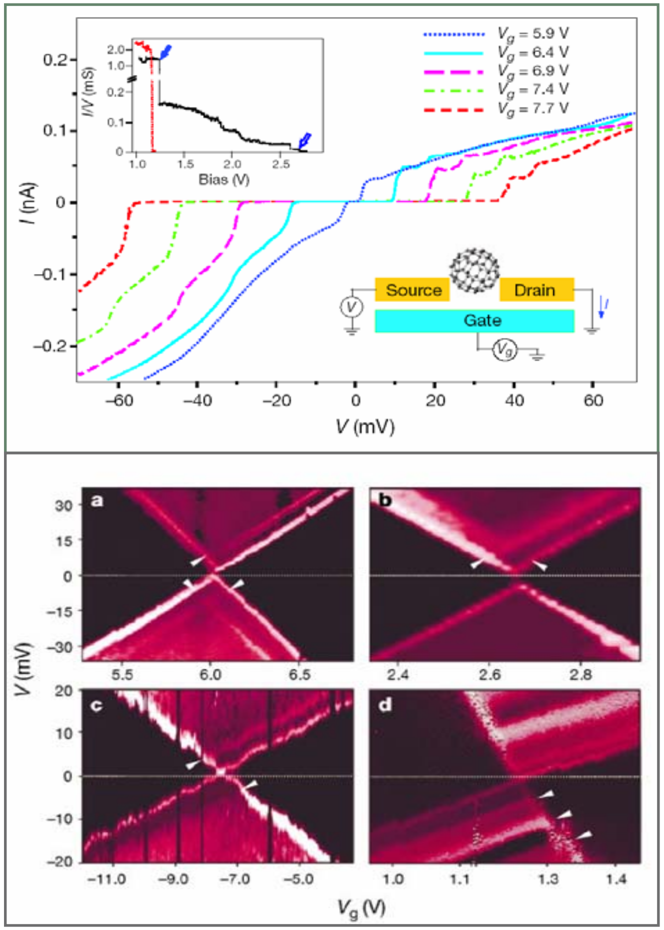
Karsten Flensberg

Nano-Science Center
Niels Bohr Institute

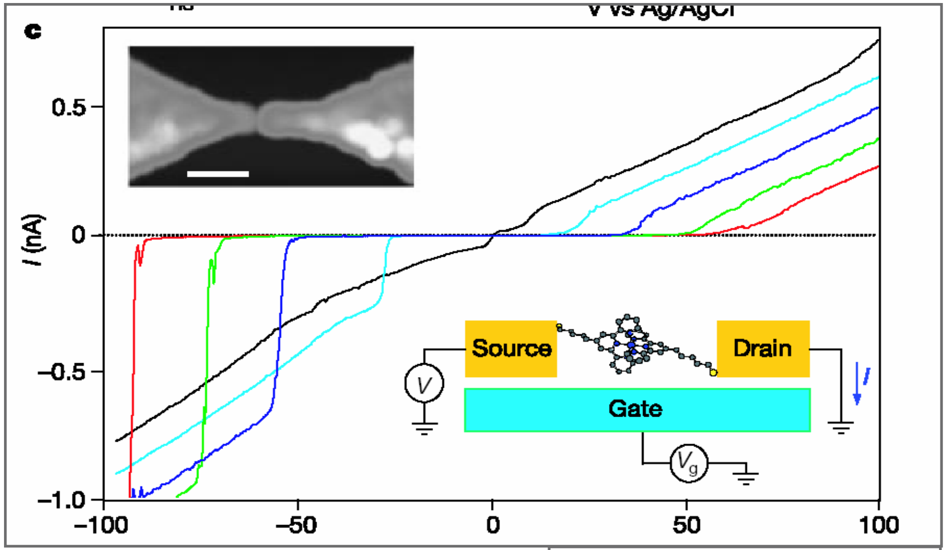
Outline

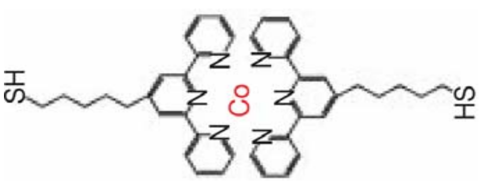
- Introduction: experimental motivation
- Franck-Condon physics
- Broadening of Franck-Condon steps – C_{60}
- Strong coupling
- Kondo effect
- Internal molecular vibrations – C_{140}
- Conclusions

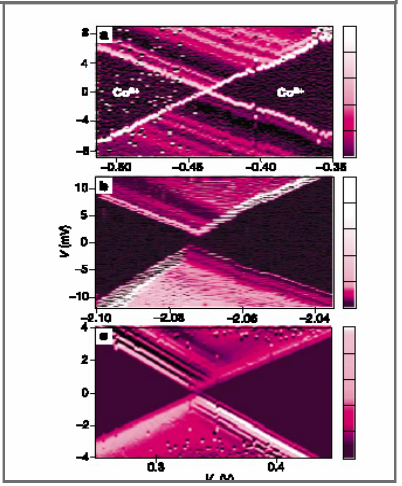
Experimental examples of single-molecule devices with electron-vibron coupling



Park et al. Nature **407,** 57 (2000)

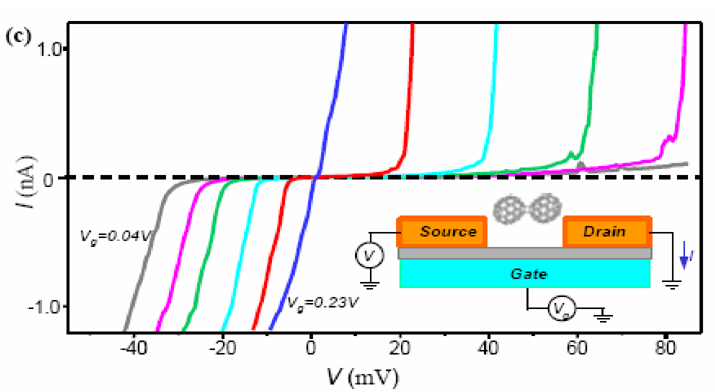


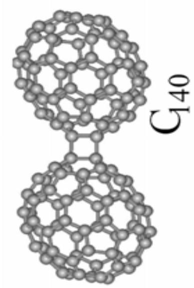


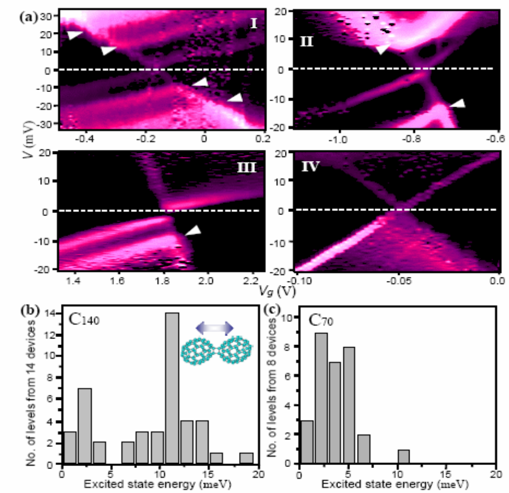


More experiments and many more ...

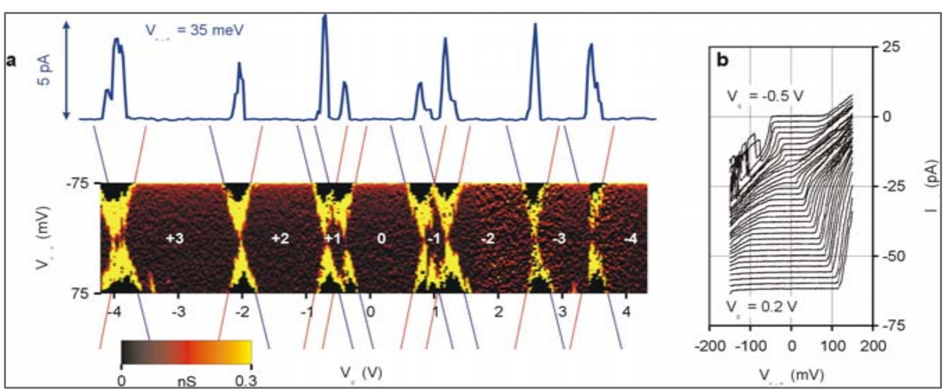
Pasupathy et al., Nano Lett. 05

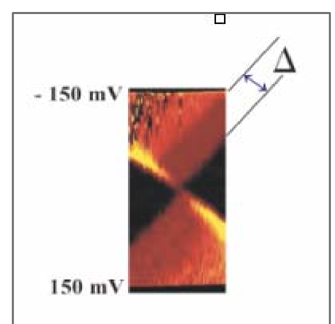


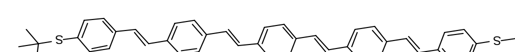




Kubatkin et al., Nature 2003.





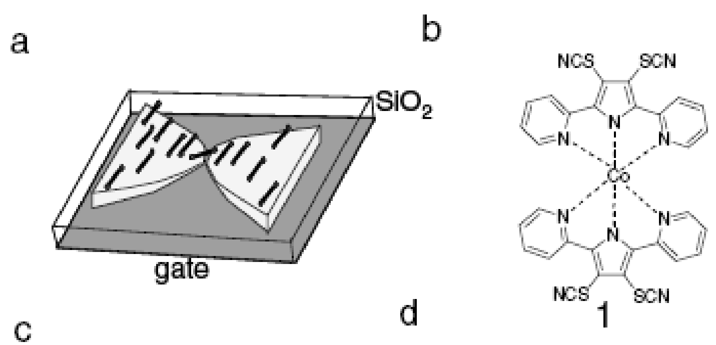


Single-molecule transistors vibrations and Kondo effect

PRL **93,** 266802 (2004) PHYSICAL REVIEW LETTERS week ending 31 DECEMBER 2004

Inelastic Electron Tunneling via Molecular Vibrations in Single-Molecule Transistors

L. H. Yu,[1] Z. K. Keane,[1] J. W. Ciszek,[2] L. Cheng,[2] M. P. Stewart,[2] J. M. Tour,[2] and D. Natelson[1,3]



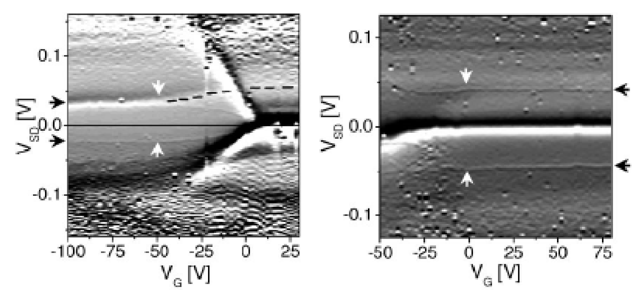


FIG. 3. Maps of $\partial^2 I_D/\partial V_{SD}^2$ as a function of V_{SD} and V_G at 5 K

In-elastic electron transfer spectroscopy (IETS)

Lee and Ho, Science 1999.

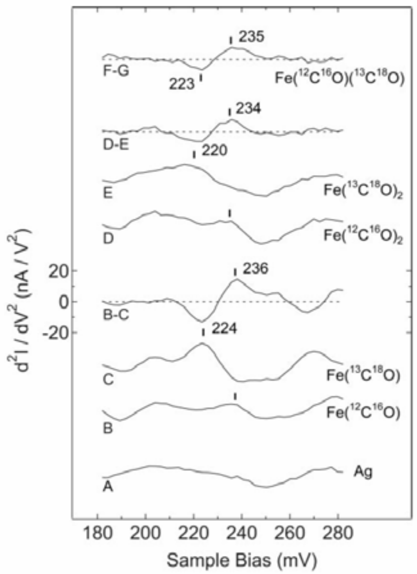
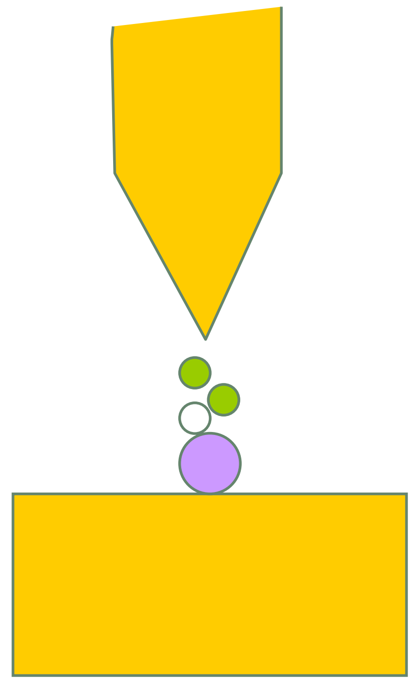
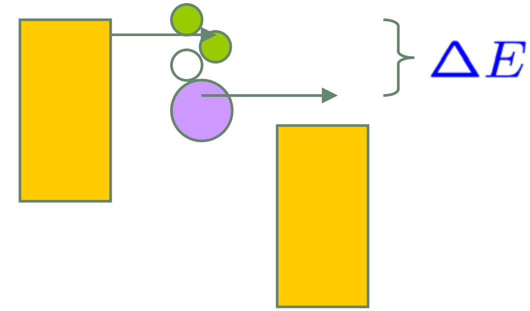


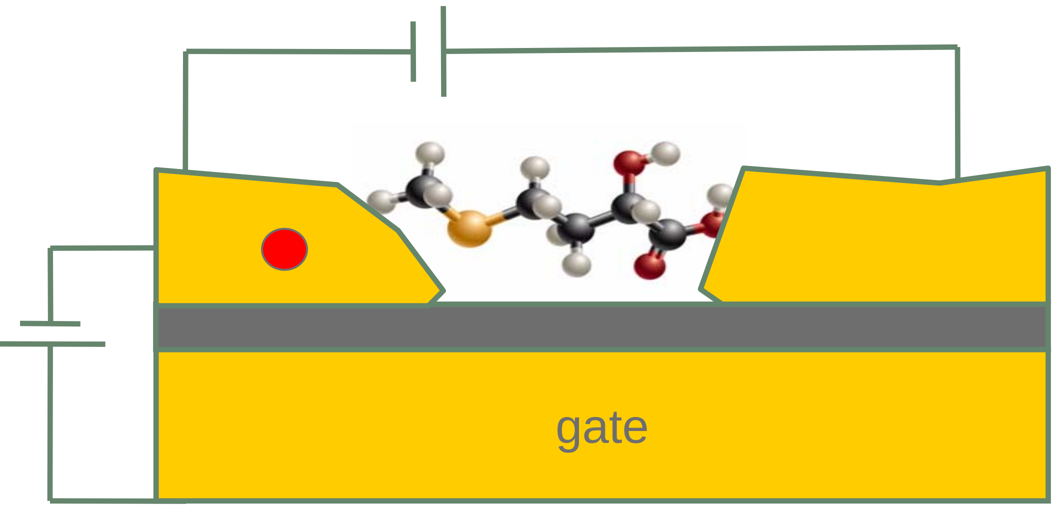
Fig. 3. Single-molecule vibrational spectra obtained by STM-IETS, showing the C–O stretch of Fe(CO) and Fe-(CO)$_2$. The differential change of the ac conductance as a function of the sample bias (d^2I/dV^2) is displayed. For each scan, the dc sample bias was ramped from 180 to 280 mV and back down in 2.5-mV steps with a 300-ms dwell time per step (1 meV = 8.065 cm^{-1}). Each spectrum has been signal averaged with repeated scans. The root-mean-square ac modulation at 200 Hz was 7 mV. Peak positions have an uncertainty of ±1 meV. (Line A) Spectrum taken over clean Ag(110) surface and signal averaged with 100 scans. (Line B) Spectrum averaged with 210 scans over the edge of the lobe in the image of single-molecule Fe($^{12}C^{16}O$). (Line C) Spectrum averaged with 210 scans over the edge of the lobe in the image of Fe($^{13}C^{18}O$). (Line B-C) Difference between spectra B and C. (Line D) Spectrum averaged with 100 scans over the left protrusion in the STM image of the single-molecule Fe($^{12}C^{16}O$)$_2$. (Line E) Corresponding spectrum averaged with 100 scans for Fe($^{13}C^{18}O$)$_2$. (Line D-E) Difference between spectra D and E. (Line F-G) Difference between spectra recorded separately over the left ($^{12}C^{16}O$, 697 scans) and right ($^{13}C^{18}O$, 280 scans) protrusions in the STM image of the single-molecule Fe($^{12}C^{16}O$)($^{13}C^{18}O$). Dashed lines denote zero level in difference spectra.





and many more!

Theoretical model



Energy/time scales:

- Γ tunneling density of states
- γ life-time of oscillations
- E_d displacement energy of oscillator
- ω_0 oscillator frequency

- ε level spacing in molecule
- U Coulomb interaction energy

Hamiltonian: $$H = H_{\text{leads}} + H_{\text{mol}} + H_{\text{tun}}$$

$$H_{\text{mol}} = \sum_i \varepsilon_i n_i + \sum_{ij} n_i n_j U_{ij} + \sum_{ij} \lambda_{ij} n_i \hat{x}_j + H_{\text{vibr}}$$

Theoretical approaches for transport with electron-vibron coupling

- Tunneling formalism and rate equations

Jonson, PRB 1989
Boese and Schoeller, EPL 2001
Braig and Flensberg, PRB 2003
Mitra, Aleiner, Milles, PRB 2004
Koch and von Oppen, PRL 2005
Nowack, Wegewijs NJP 2005
Zazunov, Feinberg, Martin PRB 2006
...

- ”In-elastic” Landauer-Büttiker formalism (weak coupling) (IETS)

$$I = \int dE \int dE'\, T(E,E') \left[f_L(E)(1 - f_R(E')) - f_R(E)(1 - f_L(E')) \right]$$

Mujica, Kemp, Ratner, JCP 1994
Troise, Ratner, Nitzan JCP 2003
...

- Single-electron scattering problem, no Fermi-sea (exact solution)

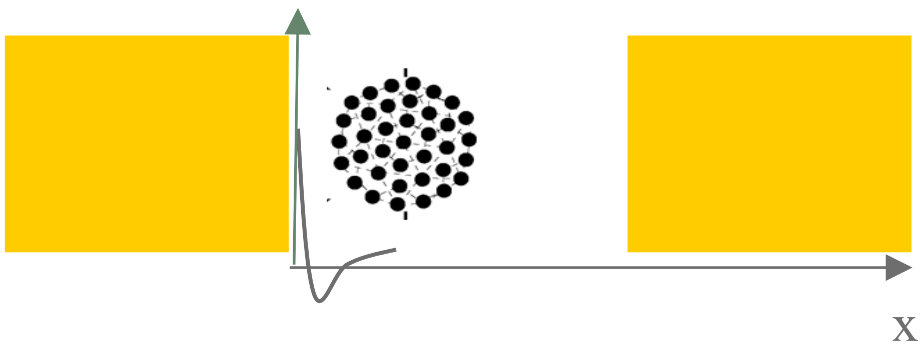
Glazman and Shekhter, JETP 88
Wingreen, Jacobsen, Wilkins, PRB 89
Bonca, Trugman PRL 97
...

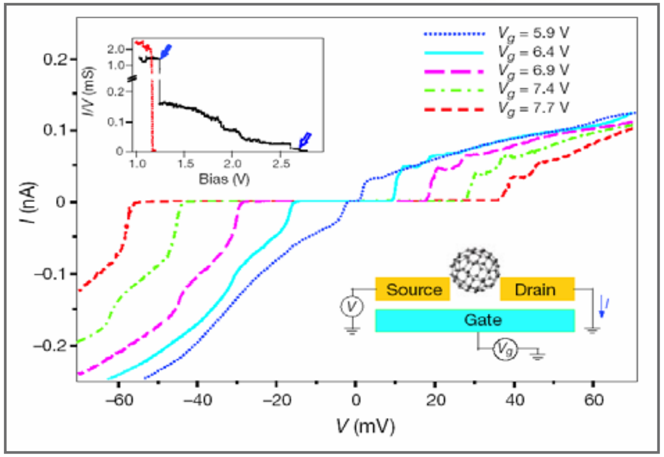
- Non-perturbative many-electron approaches

Flensberg, PRB 2003 (equation of motion)
Galperin, Nitzan, Ratner, JPC 2004 (SCBA)
Ryndyk et al. 2005 (SCBA)
Galperin, Nitzan, Ratner, PRB 2006 (equation of motion)
Frederiksen, Brandbyge, Lorente, Jauho, PRL 2004 (DFT-SCBA)
Mitra, Aleiner, Milles, PRB 2004
...

- NRG, ...

Park C_{60} experiment: Franck-Condon physics





Van der Waals interactions
Oscillator frequency: 5 meV = 1 THz
Oscillator length: 0.2 pm
Position dependence of tunneling: exp(-x κ) ~ 1, κ =1/(2 nm)

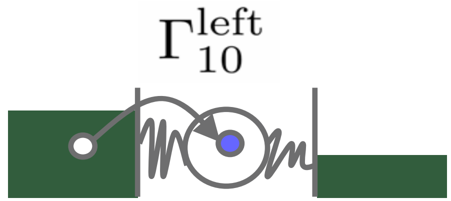
Tunneling rates: Γ = I/e = 0.1 nA/e = 10 GHz << oscillator frequency

Sequential tunneling regime: ħ Γ = 60 mK << T
Non-equilibrium phonons ?

oscillator frequency = 100 tunneling frequency

Not if Q-factor is less than 100

Weak tunneling: Rate equations



$$\frac{dP_0}{dt} = -P_0\Gamma_{10} + P_1\Gamma_{01} = 0 \quad \Longrightarrow \quad \boxed{\begin{aligned} P_1 &= \frac{\Gamma_{10}}{\Gamma_{10}+\Gamma_{01}} \\ I &= -e\left(P_0\,\Gamma_{10}^{\text{left}} - P_1\,\Gamma_{01}^{\text{left}}\right) \end{aligned}}$$

Fermi's golden rule:

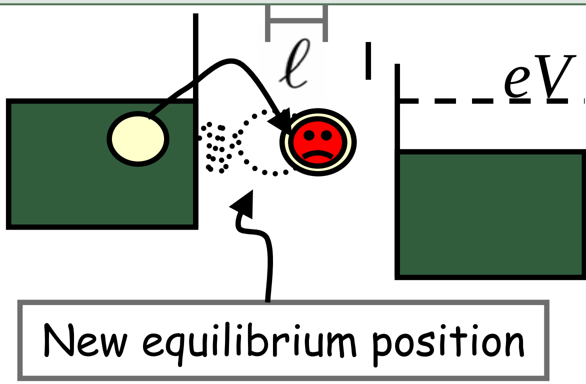
$$\Gamma_{10}^{\text{left}} = \frac{2\pi\Gamma^l}{\hbar}\sum_{i,\,f}\left|\langle f|e^{i\hat{p}\ell}|i\rangle\right|^2 \frac{e^{-E_i/kT}}{Z_0}\; n_F(\epsilon_0 + E_f - E_i - eV_l)$$

displacement operator

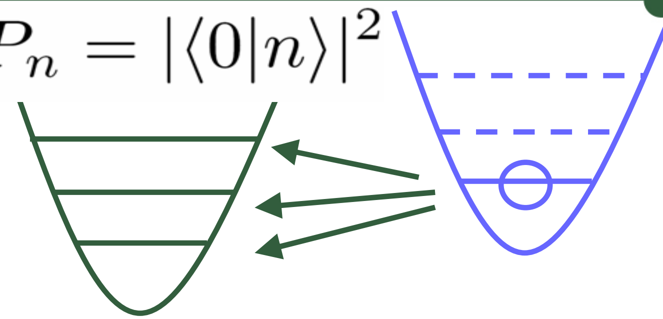
thermal distribution of $|i\rangle$

Fermi function

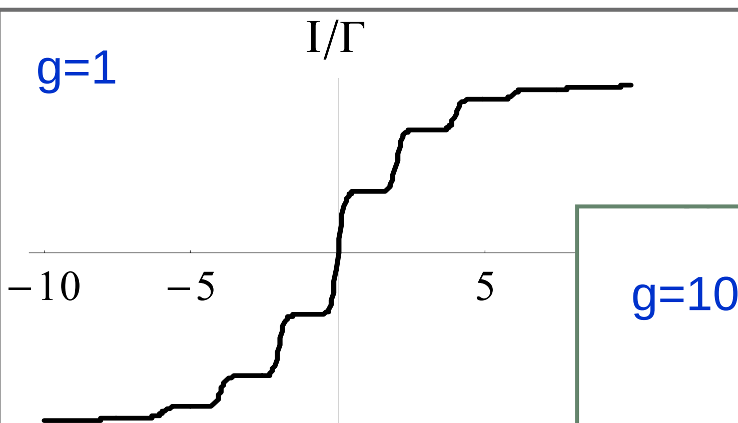
Franck-Condon steps in IV curves

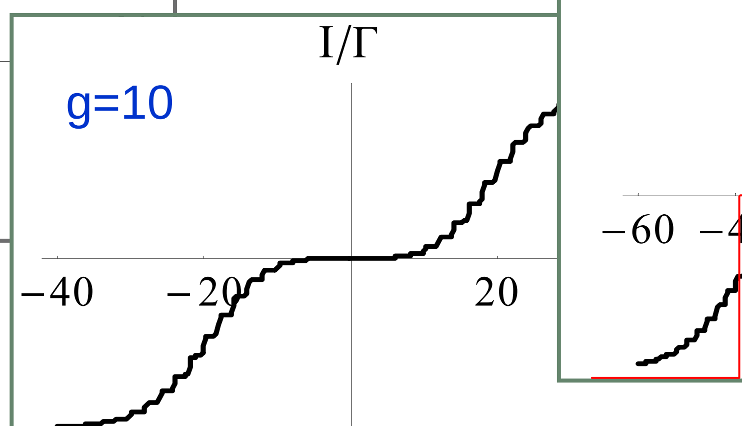


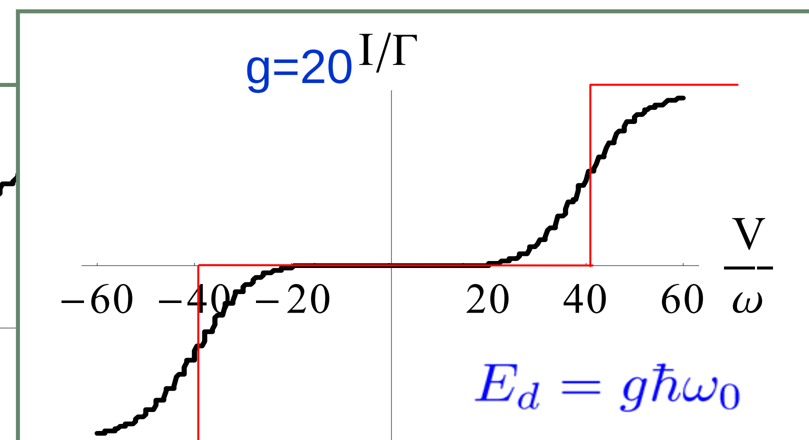
$$P_n = |\langle 0|n\rangle|^2$$



$$P_n(g) = \frac{e^{-g} g^n}{n!}, \quad g = \frac{1}{2}\left(\frac{\ell}{\ell_0}\right)^2, \quad \ell_0^2 = \frac{\hbar}{m\omega_0}$$



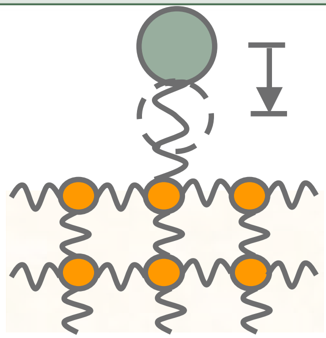




$$g = \frac{P_1(g)}{P_0(g)}$$

Coupling to dissipative environments

(Braig and KF, PRB 2003)



$$x \longrightarrow x - \ell$$

$$y_i \longrightarrow y_i - \ell_i$$

$$P_{fi} = |\langle f|\text{displacement}|i\rangle|^2$$

$$\boxed{P(E_f - E_i)}$$

$$P(E) = \int_{-\infty}^{\infty} e^{iEt/\hbar} \exp\left(\frac{2g}{Q\pi}\int_{-\infty}^{\infty}\frac{d\omega}{\omega}\,\frac{e^{-i\omega t}-1}{1-e^{-\hbar\omega/kT}}\,\frac{\omega_0^4}{(\omega^2-\omega_0^2)^2+\omega_0^2\omega^2/Q^2}\right)$$

Related to classical response function! (Feynman-Vernon)

New rate equations:

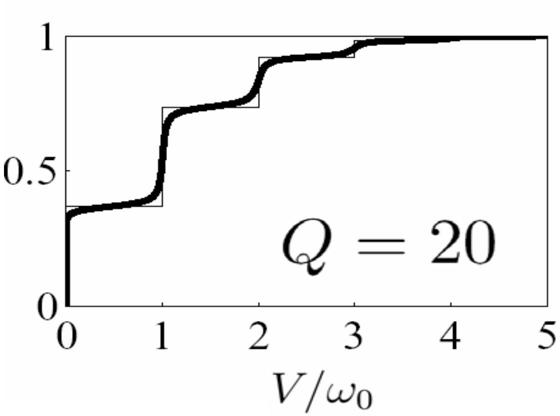
$P(E)$ replaces the discrete Franck-Condon function $P_n(g)$

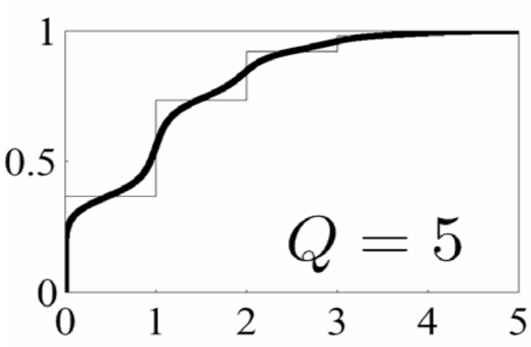
Similar to electromagnetic environment theory for Coulomb blockade (Ingold and Grabert, Europhys. Lett. 14, 171 (91)).

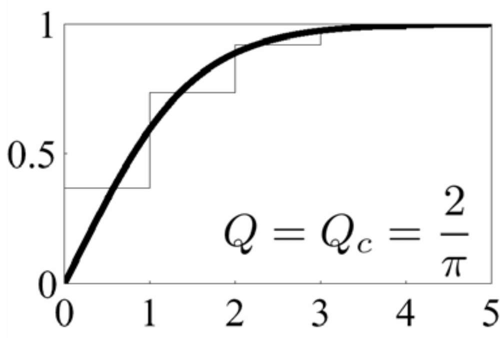
From Franck-Condon blockade to phonon blockade

$$kT = 0 \quad g = 1$$

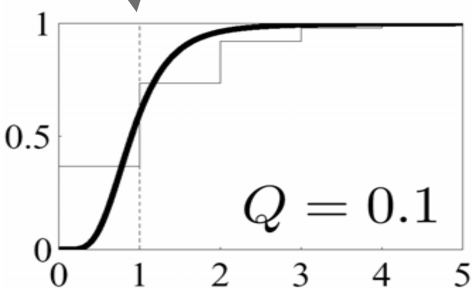
Power law at small energies: $V^{2g/Q\pi}$

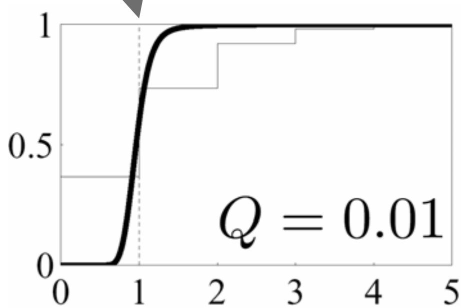


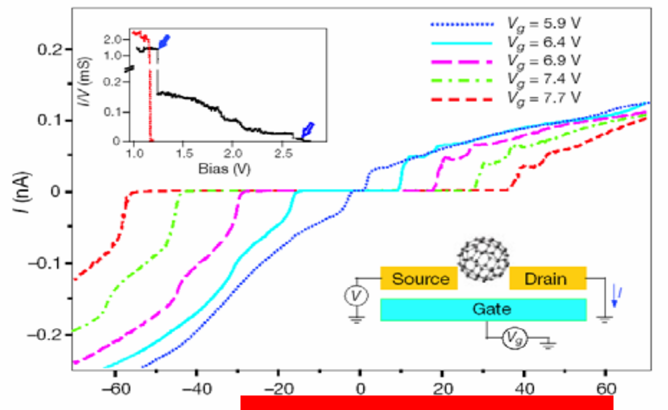




Classical displacement energy



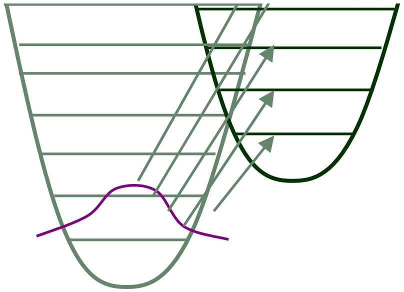


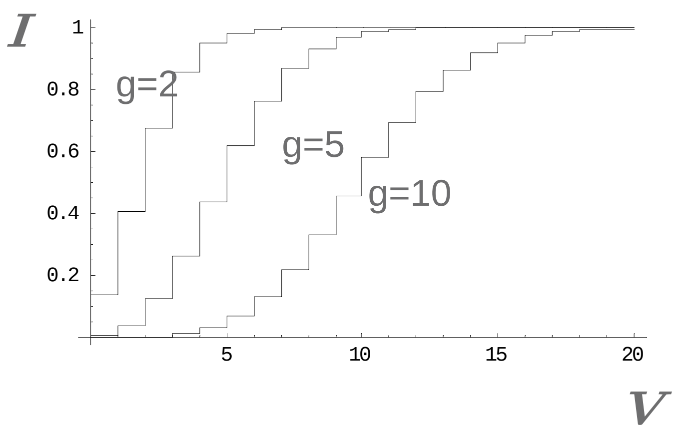


$Q = 5\text{-}10$

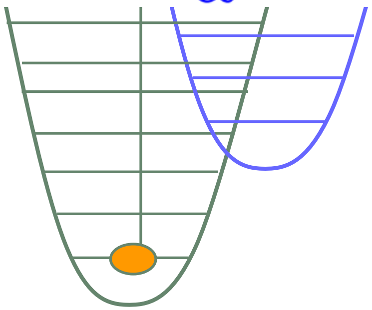
From Franck-Condon blockade to phonon blockade II

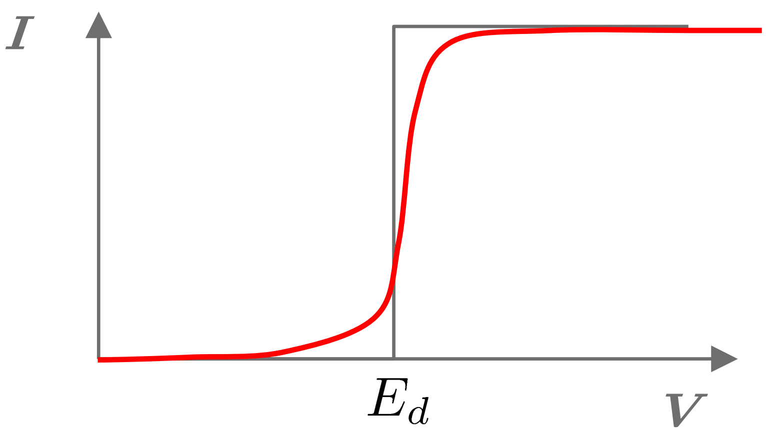
$$\frac{Q}{\omega_c} \gg \frac{\hbar}{E_d} = \frac{\hbar}{g\hbar\omega_c}$$





$$\frac{Q}{\omega_c} \ll \frac{\hbar}{E_d} = \frac{\hbar}{g\hbar\omega_c}$$





Detailed modeling of Park C_{60} experiment

Lagrangean:

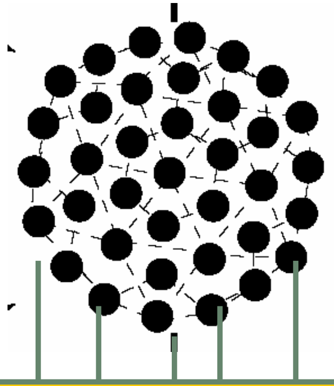
$$\mathcal{L}(\vec{r},t) = \frac{1}{2}\rho\left[(\partial_t\vec{u})^2 - (v_l^2 - 2v_t^2)\left(\vec{\nabla}\vec{u}\right)^2 - v_t^2(\vec{\nabla}\times\vec{u})^2 - 2v_t^2\frac{\partial u_i}{\partial x_j}\frac{\partial u_j}{\partial x_i}\right]$$

Force:

$$\mathcal{F} = k_M\left[x - \int_0^\infty 2\pi r f(r) u_z^0(r) dr\right]$$

Boundary conditions:

$$T_{zr}\big|_{z=0} = 0, \qquad T_{zz}\big|_{z=0} = -\mathcal{F}f(r)$$

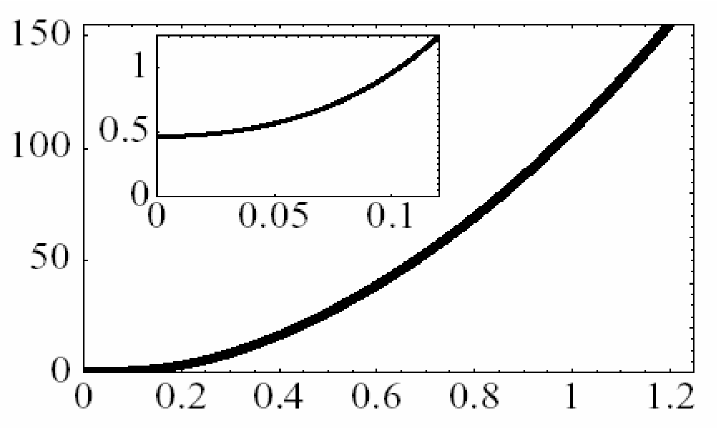


$f(r)$

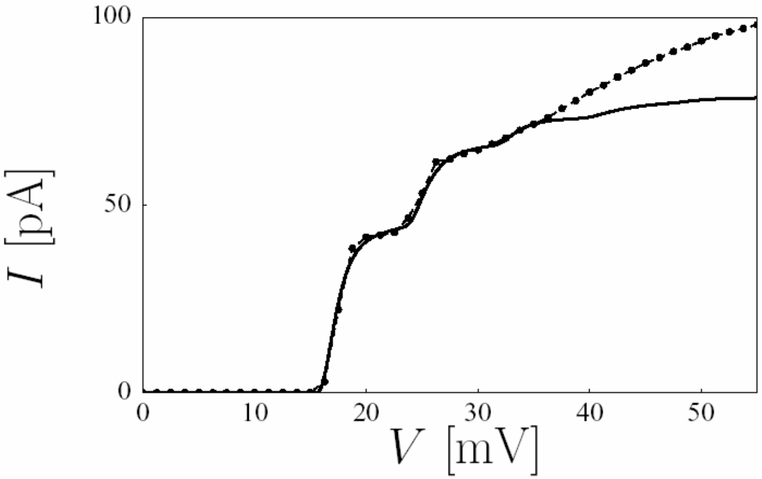
SCIENCE
UNIVERSITY OF COPENHAGEN

Frequency dependent Q-factor

Frequency dependence of Q

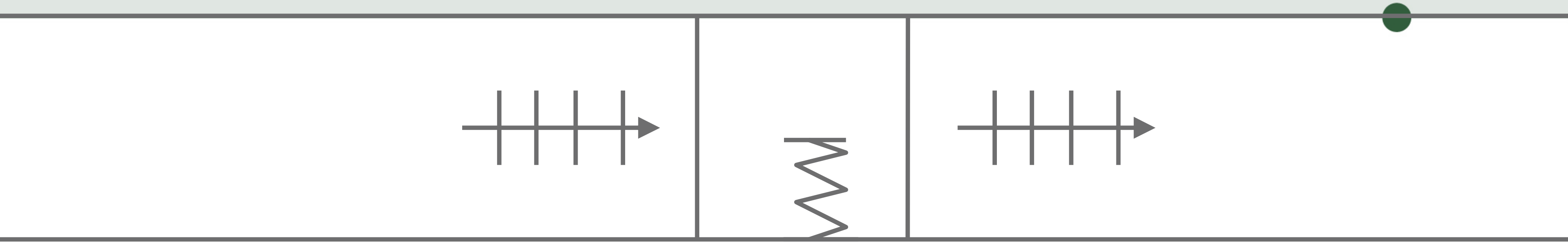


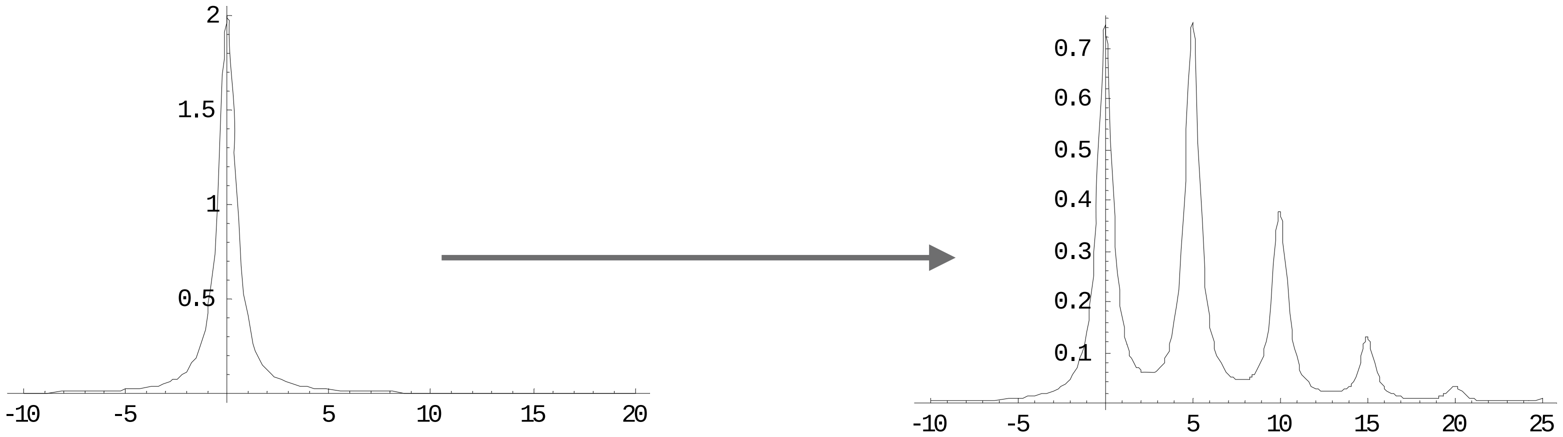
IV curves fitted to C_{60} experiment



Fit parameters: left and right tunneling rates.
Fixed parameters: elastic coefficient of Au
Determined from experiments: oscillator frequency and size of molecule

Resonant tunneling and electron-vibron coupling



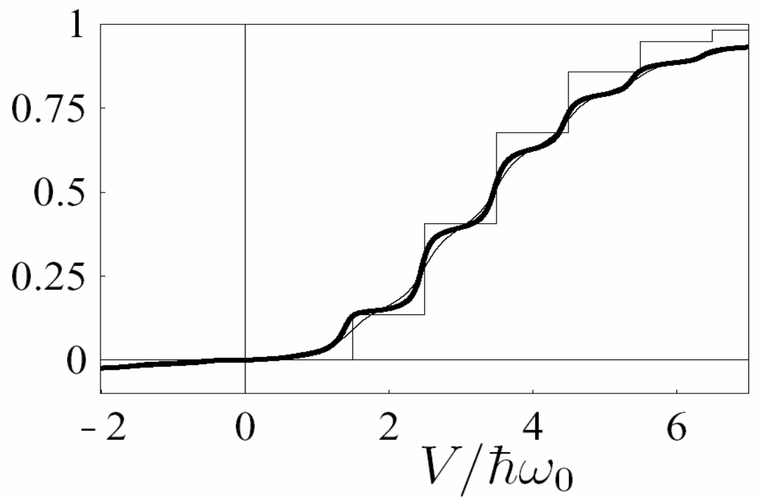


$$G^R(d,t) \rightarrow G^R(d,t)\exp\left[g\left(e^{i\omega_o t}-1\right)\right]$$

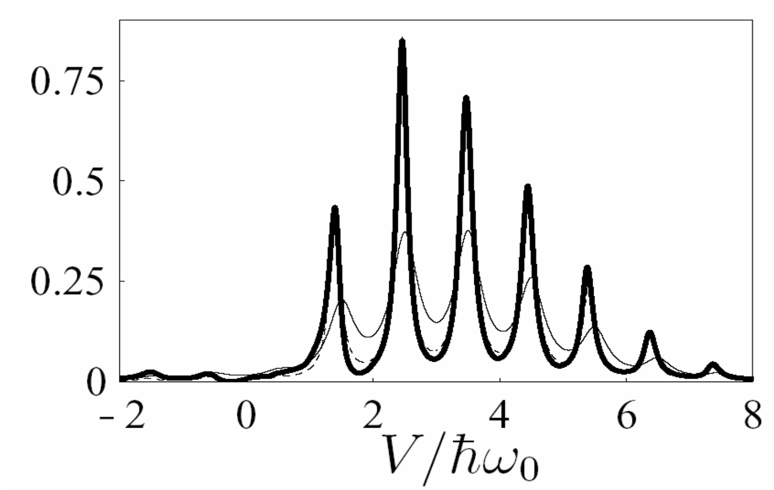
Glazman-Shehkter, 1988 Wingreen, Jacobsen, Wilkins, 1989

With Fermi sea – sidebands even sharper

Current



dI/dV



$$
\begin{aligned}
g &= 2 \\
\frac{\Gamma}{\hbar\omega_0} &= 0.5 \\
\varepsilon_0 &= 1.5\hbar\omega_0
\end{aligned}
$$

KF, PRB 2003

Kondo resonance with electron-vibron coupling

Question:

- Is the Kondo effect destroyed by coupling to phonons?

  as with external ac field, Kaminski, Nazarov, Glazman, PRB 2000

- If not, can one expect Kondo sidebands?

  as with ac fields, see Kogan *et al.* Science **304**, 1293 (04)

From Anderson-Holstein model to Kondo model

Anderson-Holstein model

$$
\begin{aligned}
H &= \hbar\omega b^\dagger b + \lambda(n_\uparrow + n_\downarrow)(b + b^\dagger) \\
&+ \xi_d(n_\uparrow + n_\downarrow) + U n_\uparrow n_\downarrow \\
&+ \sum_{k\sigma\alpha} \xi_{k\sigma} c^\dagger_{k\sigma\alpha} c_{k\sigma\alpha} + \sum_{k\sigma\alpha} t_{k\alpha} d^\dagger_\sigma c_{k\sigma\alpha} + \mathrm{h.c}
\end{aligned}
$$

Two canonical transformations (Schüttler, Fedro 1988) $H' = UHU^\dagger$

U =
Lang–Firsov (polaron transformation)
and generalized Schrieffer–Wolf transformation

Paaske and KF, PRL 2005

"Holstein-Kondo model"

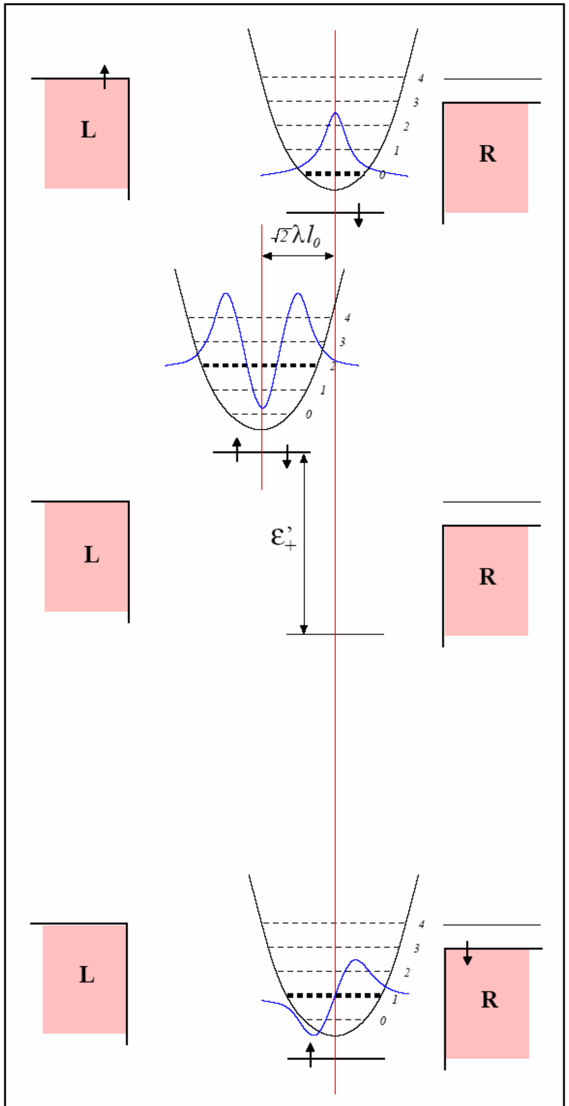
$$H'' = \sum_{\alpha,\mathbf{k},\sigma} \xi_{\alpha\mathbf{k}} c^\dagger_{\alpha\mathbf{k}\sigma} c_{\alpha\mathbf{k}\sigma} + \omega_0 b^\dagger b + \sum_{\alpha,\mathbf{k},\sigma;\alpha',\mathbf{k}',\sigma'} \mathbb{J}_{\alpha,\mathbf{k};\alpha',\mathbf{k}'} \mathbf{S}\cdot c^\dagger_{\alpha'\mathbf{k}'\sigma'} \boldsymbol{\tau}_{\sigma'\sigma} c_{\alpha\mathbf{k}\sigma}$$

Exchange coupling is now an operator in boson space

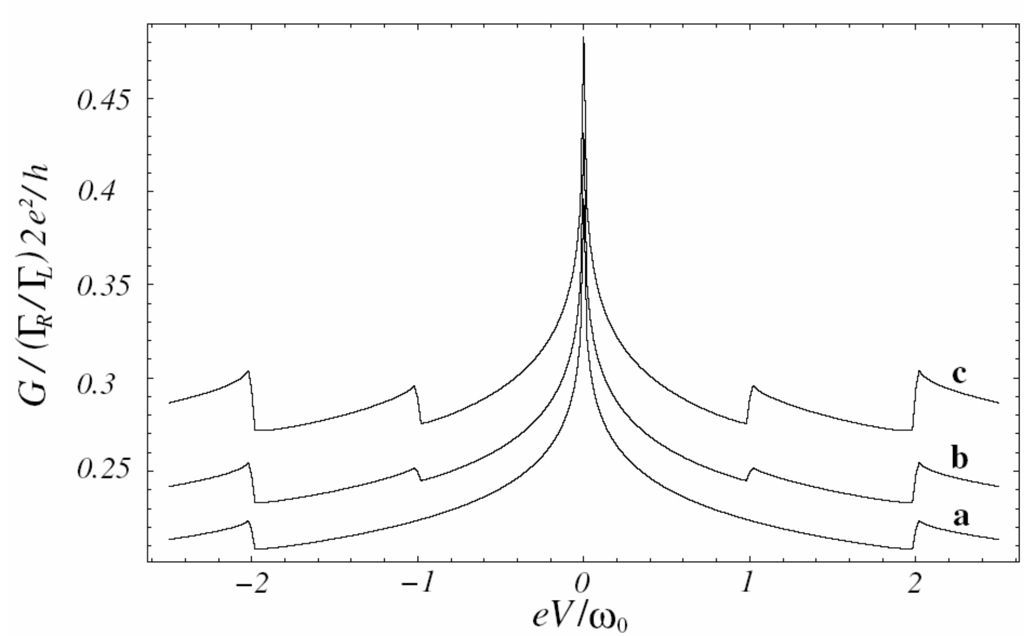
$$\begin{aligned} J^{n'n}_{\alpha',\mathbf{k}';\alpha,\mathbf{k}} &\equiv \langle n'|\mathbb{J}_{\alpha',\mathbf{k}';\alpha,\mathbf{k}}|n\rangle \\ &= t^*_{\alpha'\mathbf{k}'} t_{\alpha\mathbf{k}} \sum_{m=0}^{\infty} \Bigg\{ f_{mn'} f_{mn} \Bigg[\frac{1}{\xi_{\alpha\mathbf{k}} - \varepsilon_- + (m-n')\omega_0} \\ &\quad + \frac{1}{\xi_{\alpha'\mathbf{k}'} - \varepsilon_- + (m-n)\omega_0} \Bigg] \\ &\quad - f_{n'm} f_{nm} \Bigg[\frac{1}{\xi_{\alpha\mathbf{k}} - \varepsilon_+ - (m-n)\omega_0} \\ &\quad + \frac{1}{\xi_{\alpha'\mathbf{k}'} - \varepsilon_+ - (m-n')\omega_0} \Bigg] \Bigg\} \end{aligned}$$

$$f_{mn} = \langle m|e^{i\hat{p}\ell}|n\rangle$$

Cotunneling with vibrations

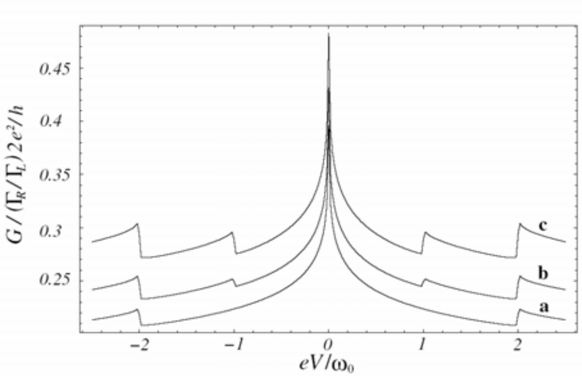


Calculate current to 3rd order in $\mathbb{J}$

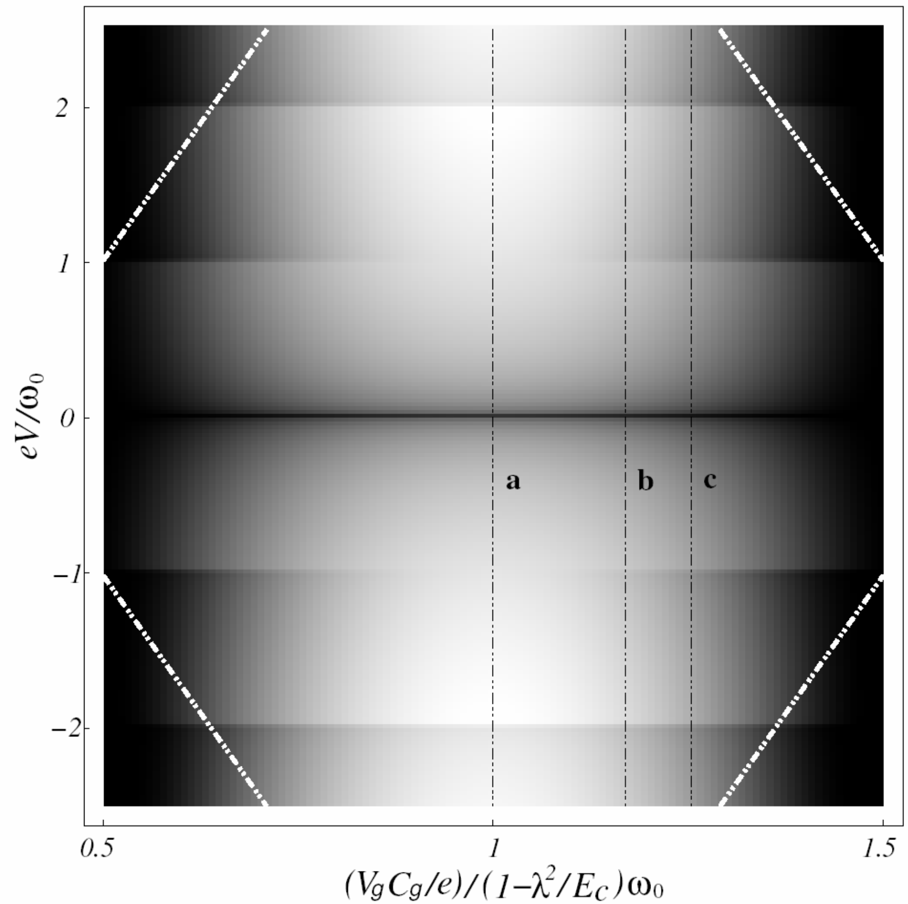


Similar curves by König, Schoeller, Schön (PRL 96).

Diamond plot (V_{sd}-V_g plot)

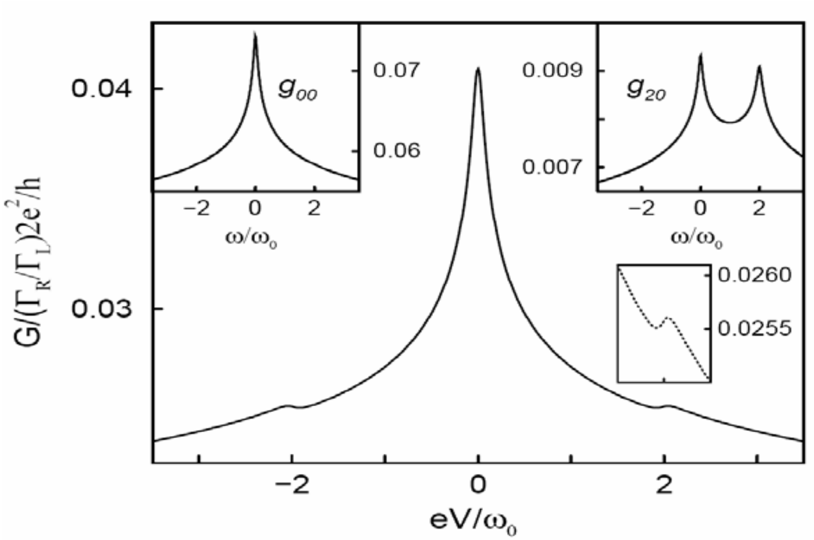


At the particle-symmetric point only even peaks are non-zero! (selection rule due parity)

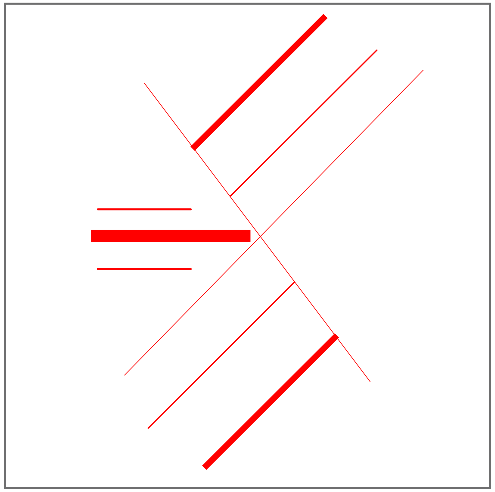


Conclusions on Kondo resonance sidebands

Poor-man's RG calculation:
Sidebands remains, but only small feature
Central peak not suppressed unlike ac-field case!



OVERALL PICTURE:



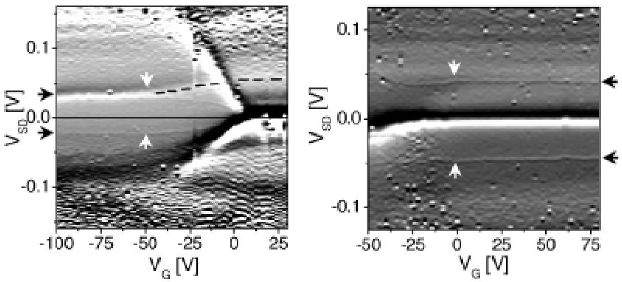
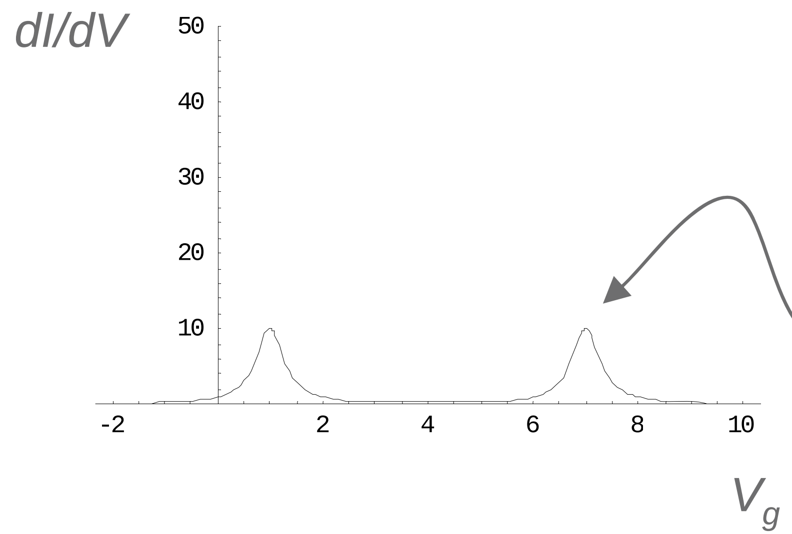


FIG. 3. Maps of $\partial^2 I_D/\partial V_{SD}^2$ as a function of V_{SD} and V_G at 5 K

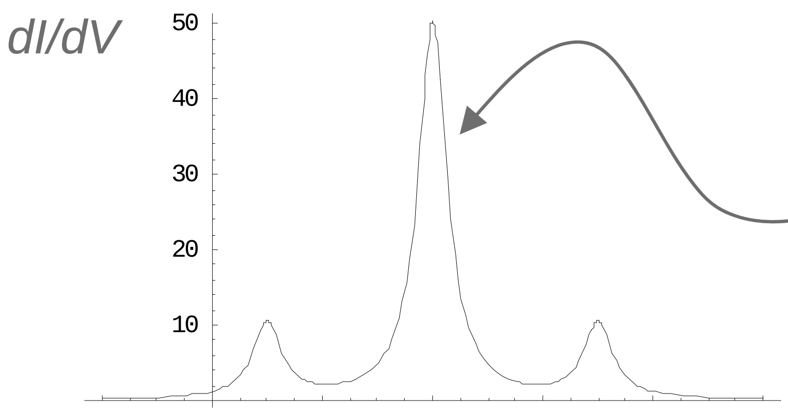
Size of Kondo peak

$\mathrm{T} > \mathrm{T_K}$



Down by $|f_{00}|^2$

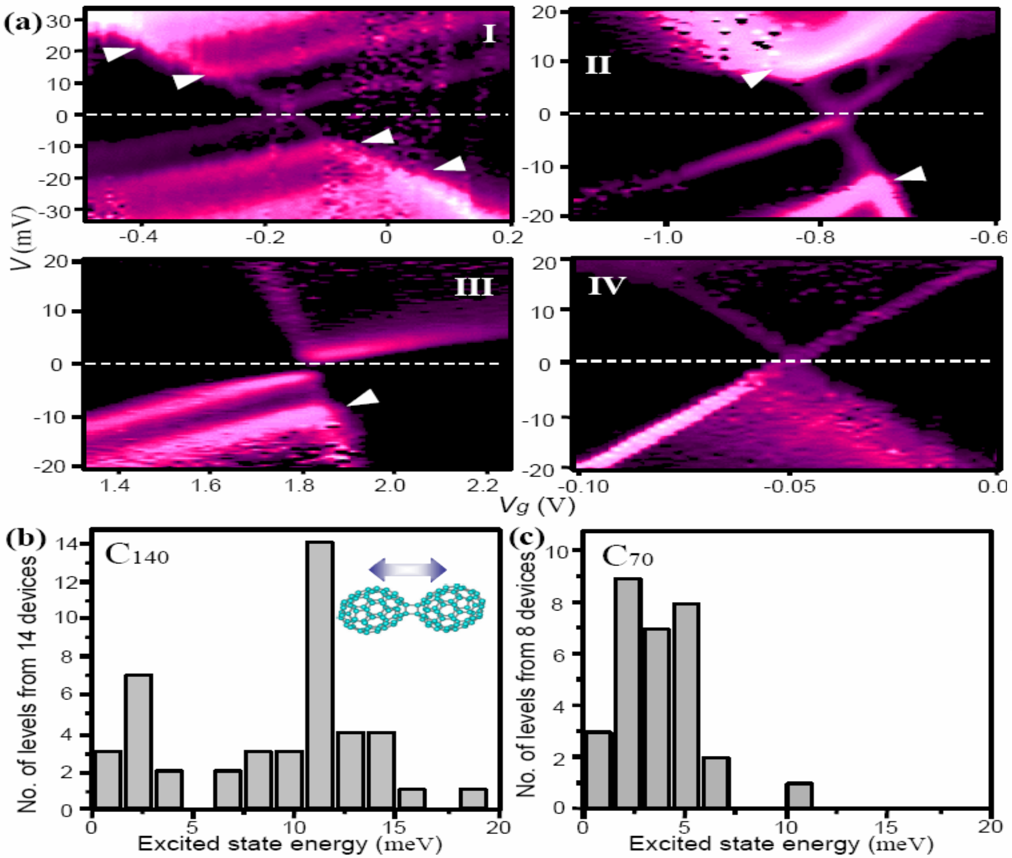
$\mathrm{T} < \mathrm{T_K}$

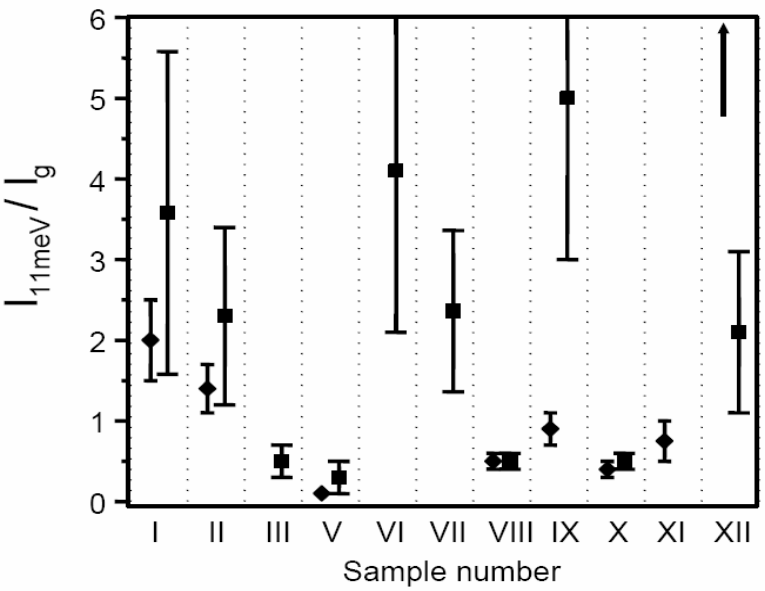


For $E_C \gg \hbar\,\omega$, J is unaffected by electron-vibron coupling

Polaron formation in dimers and transport

Pasupathy et al. (Cornell), Nano Lett. 2005

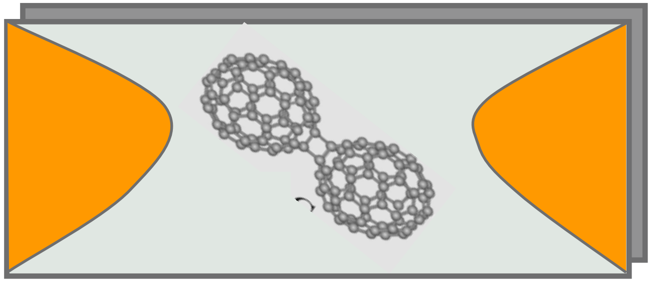


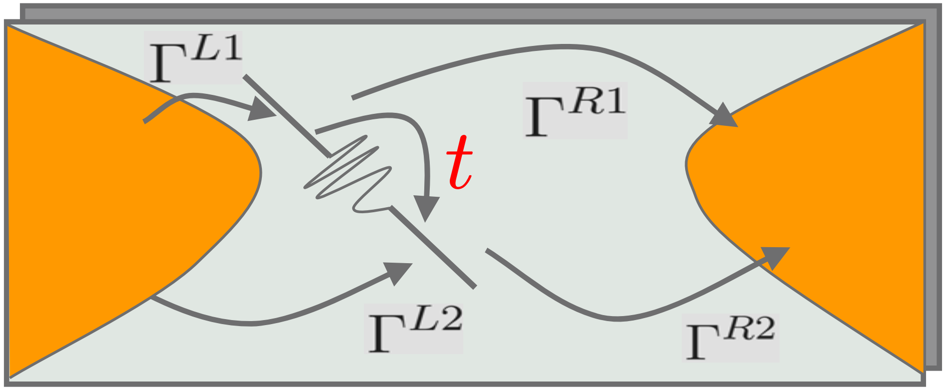


Simple dimer model

G. Kaat and KF, PRB **71**, 155408 (05)

C140 model





Boson coupled to a two-level system:

$$H_{\text{dimer}} = \frac{\hat{p}^2}{2M} + \frac{1}{2}m\omega_0^2\hat{x}^2 + (\lambda\hat{x} + \Delta)(n_1 - n_2) - t(|1\rangle\langle 2| + |2\rangle\langle 1|)$$

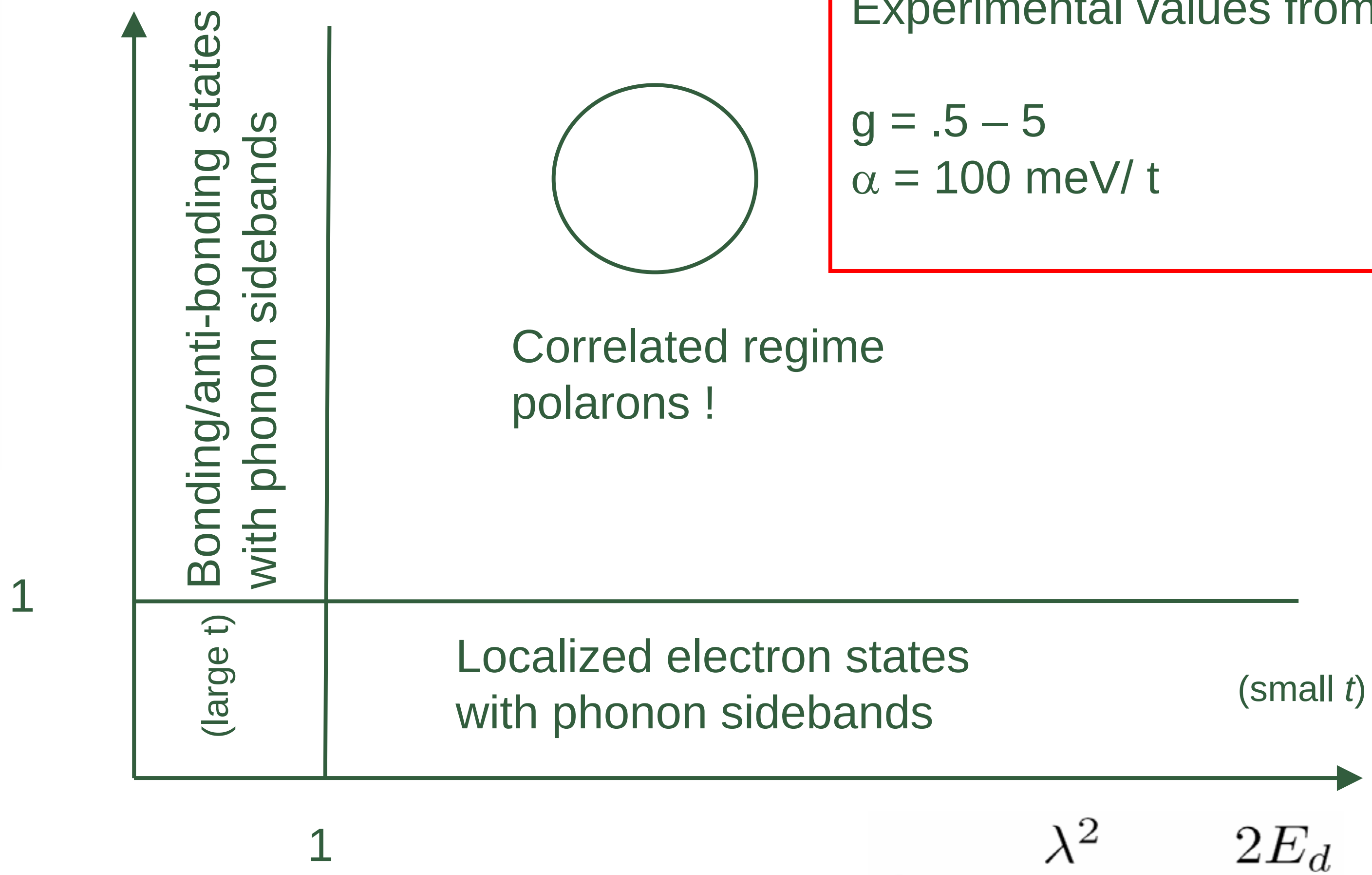
Two parameters: $g = \dfrac{\lambda^2}{2m\hbar\omega^3} = \dfrac{E_d}{\hbar\omega}$ $\alpha = \dfrac{\lambda^2}{m\omega^2 t} = \dfrac{2E_d}{t}$

Polaron localization of charge

$$g = \frac{\lambda^2}{2m\hbar\omega^3} = \frac{E_d}{\hbar\omega}$$

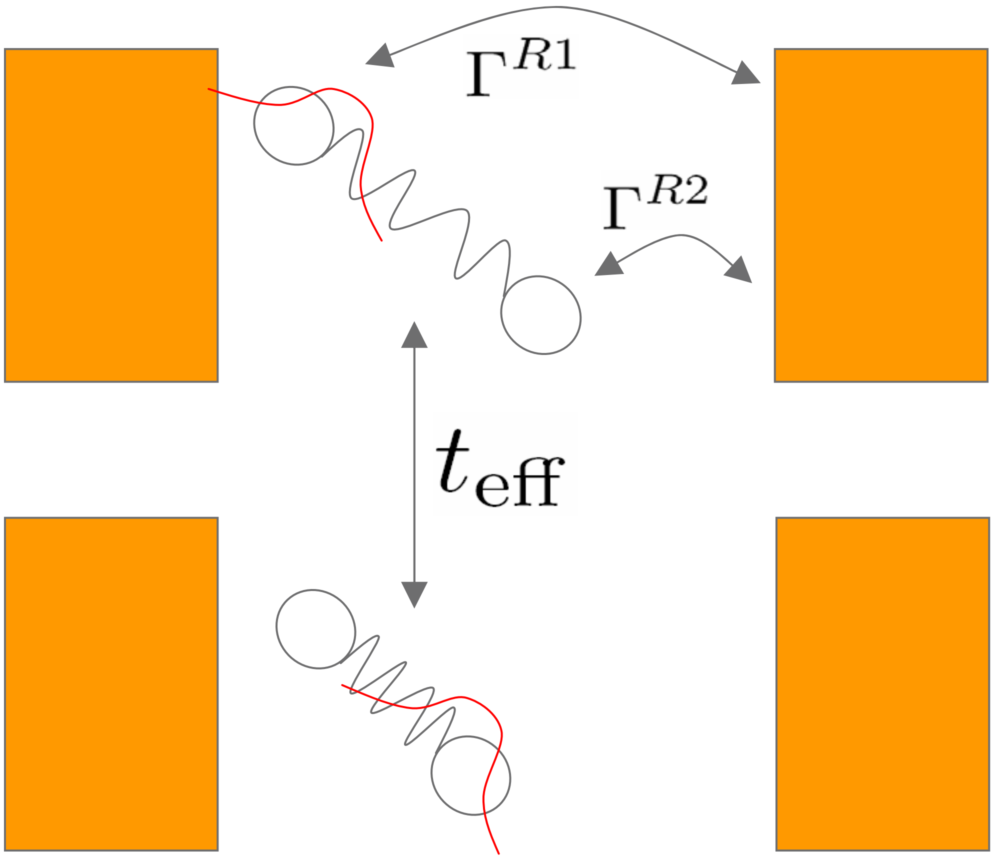
Experimental values from C_{140}:

$g = .5 – 5$
α = 100 meV/ t



$$\alpha = \frac{\lambda^2}{m\omega^2 t} = \frac{2E_d}{t}$$

Two transport regimes



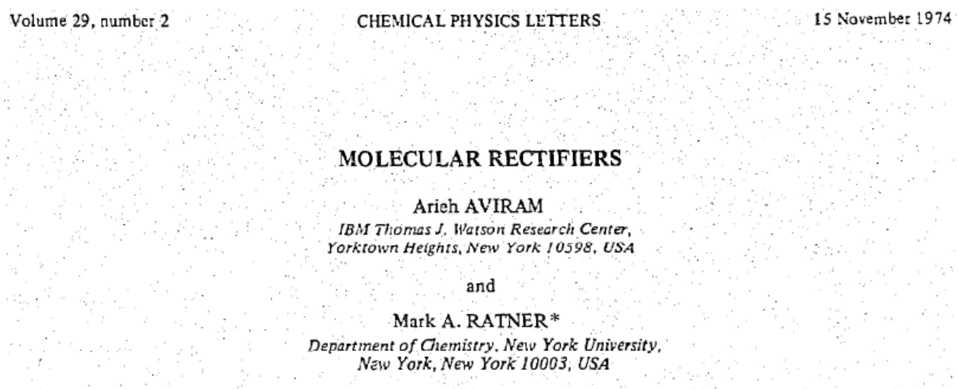
$t_{\rm eff} \gg \Gamma^{R1}$

Levels well resolved
Single ”dot” case
(usual master equation)
No (strong) asymmetry

$t_{\rm eff} \ll \Gamma^{R1}$

Levels not resolved
Double ”dot” situation
(master equation using polarons)
Strong asymmetry

Connection to Aviram—Ratner rectifier



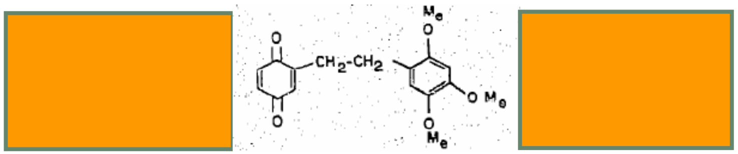
Volume 29, number 2 CHEMICAL PHYSICS LETTERS 15 November 1974

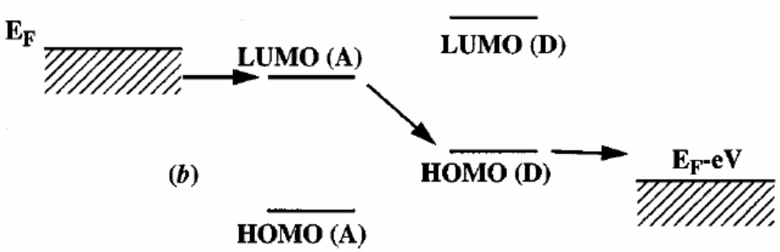
MOLECULAR RECTIFIERS

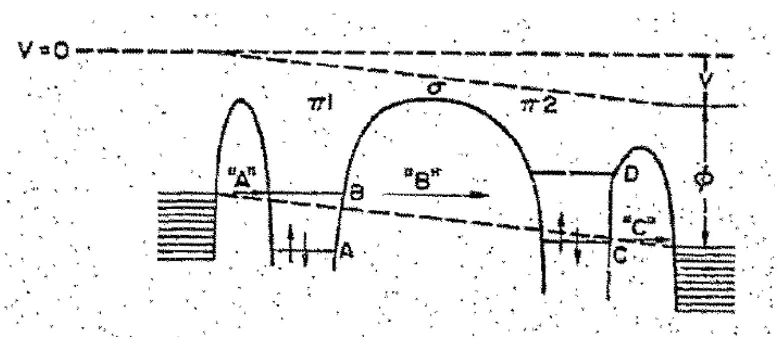
Arieh AVIRAM
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598, USA

and

Mark A. RATNER*
Department of Chemistry, New York University, New York, New York 10003, USA

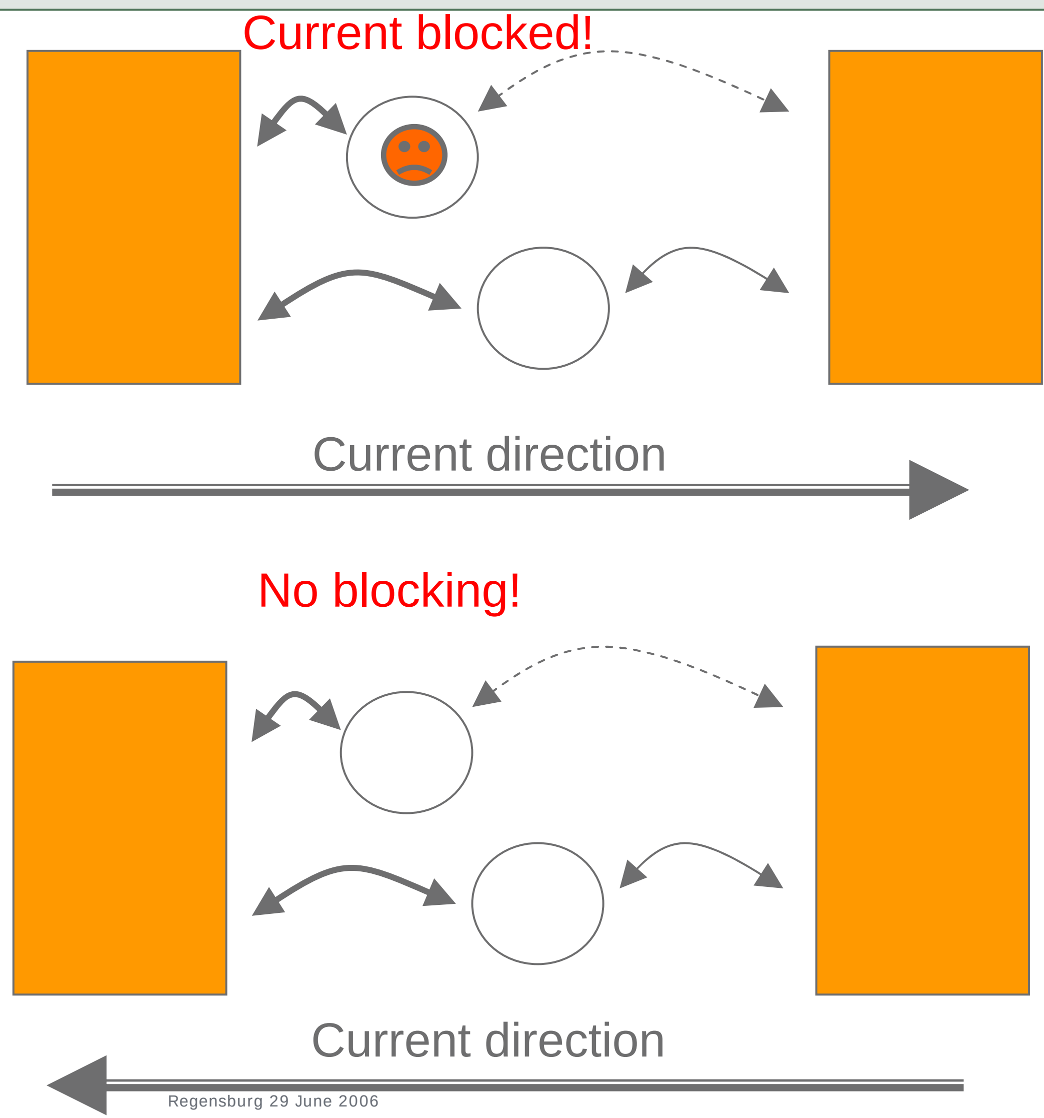


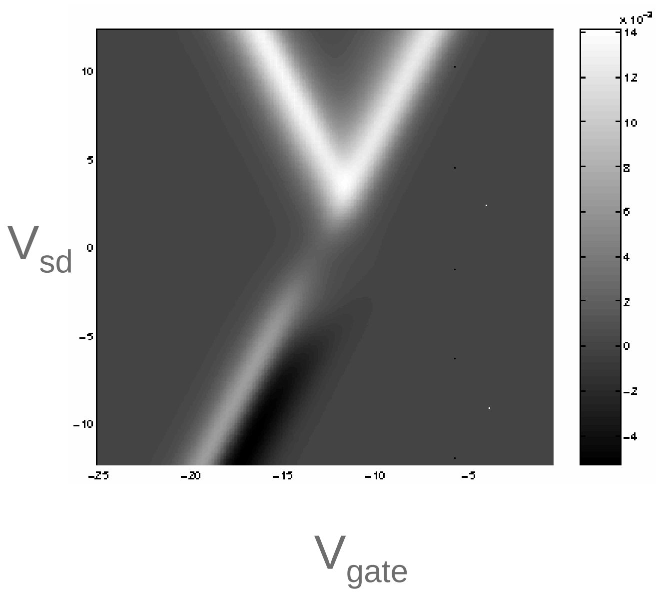




Dissipation or localization is essential !

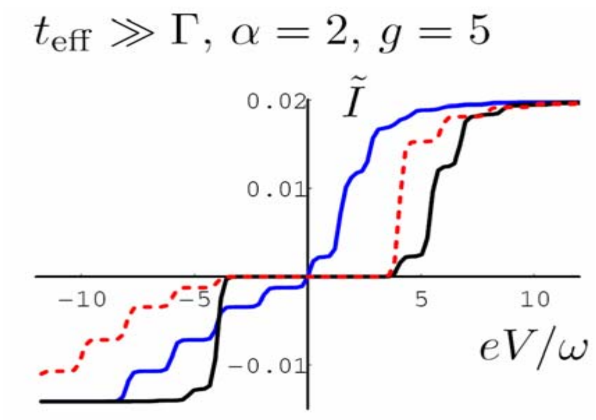
Rectification due to localization

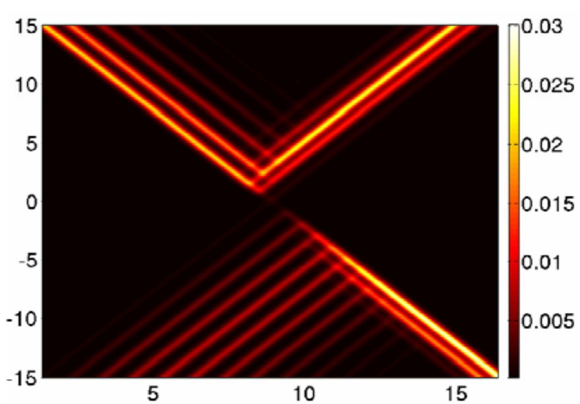




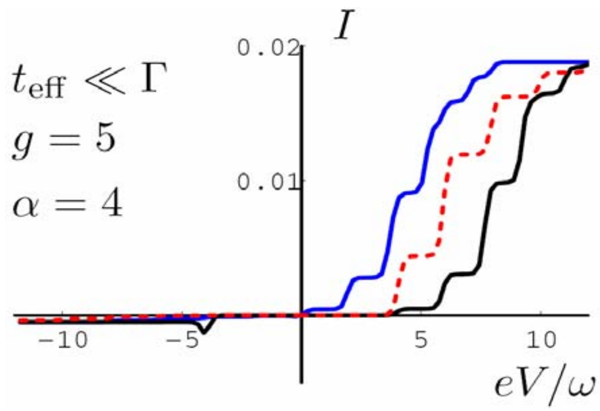
Full numerical solution of master equation in the two limits

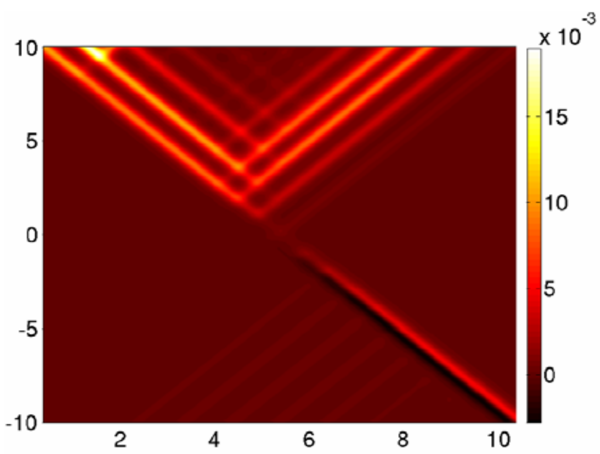
”Single dot”- theory





”Double dot” theory





CONCLUSIONS

Vibrations show up as sidebands

Shape tells about damping:

- Large Q: Current suppressed by Franck-Condon factors
- Small Q: Current suppressed by dissipation

In the Kondo regime

- Weak sidebands can be expected
- Kondo peak NOT suppressed as sequential tunneling

Dimers with internal vibrations

- Spectroscopy of molecule
- Strong internal polaron coupling and small dissipation gives strong rectification