Механизмы переноса заряда в неупорядоченных твердых матрицах, изготовленных на основе органических материалов

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Ordinary ET (polar liquid)

H_2O H_2O H_2O

$$\left(Fe^{2+}L_5^-\right)^{3-} + L^- \leftrightarrow$$
$$\leftrightarrow \left(Fe^{3+}L_6^-\right)^{3-} + e^-$$

H_2O

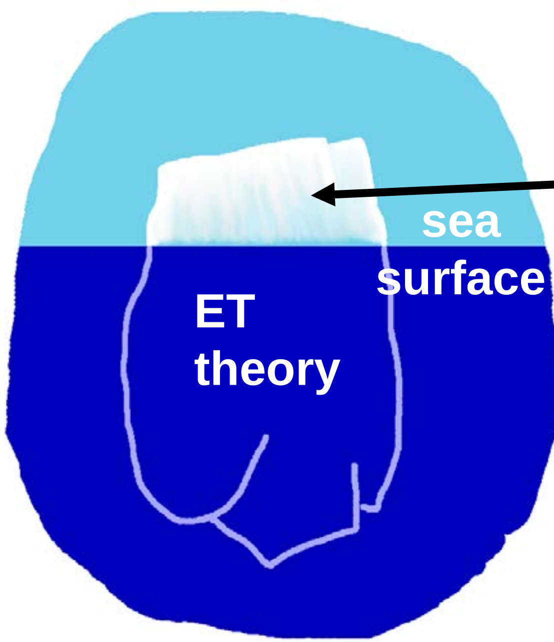
$$\varepsilon_0 = 78; \quad \varepsilon_\infty = 1.8$$

Pekar factor = $\left(\frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_0}\right) = 0.55$

$$E_r = \frac{1}{2}\left(\frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_0}\right)\left(\frac{1}{a} - \frac{2}{R_{12}}\right)$$

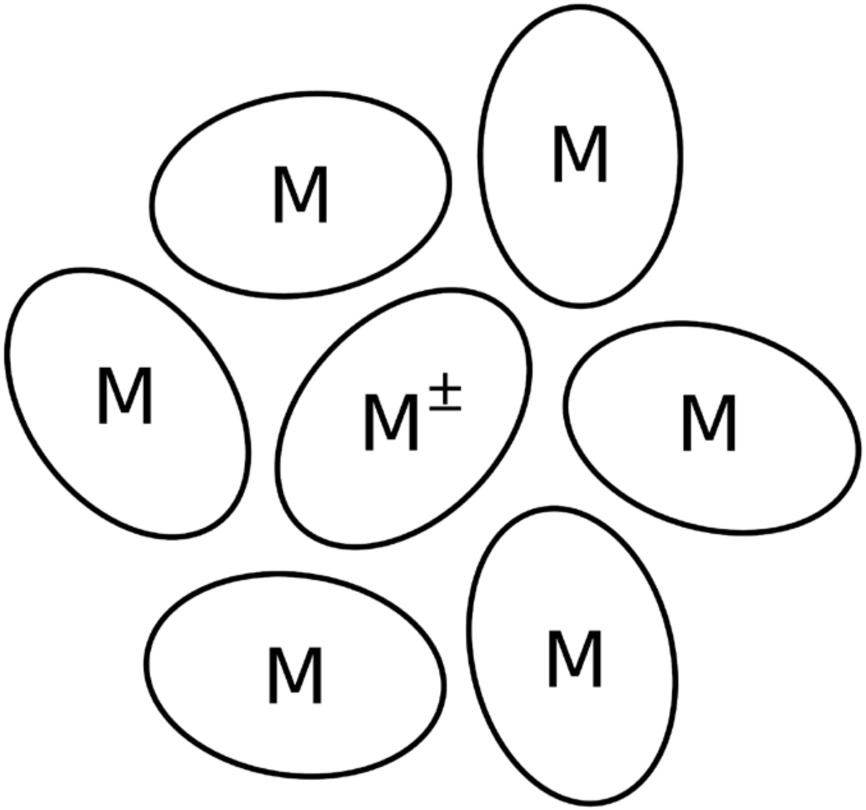
reorganization energy

Levich-
-Dogonadze
(1959)
(Theory of
multi-phonon
transitions)



Marcus (1956)
(phenomemnological)

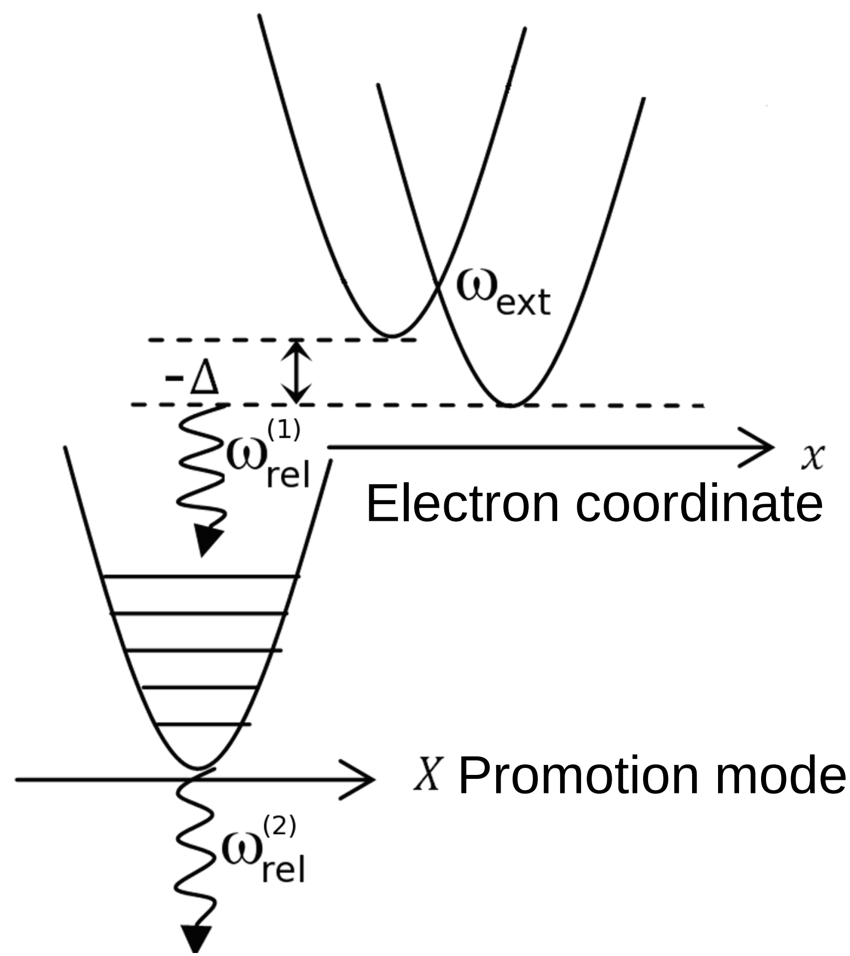
The ET scheme. The reaction center



$$M^{+}M \longrightarrow MM^{+} + \Delta$$

$$K(T) << \begin{pmatrix} \omega_{ext} \\ \omega_{rel} \end{pmatrix} << \omega_{\text{int}} \approx \omega_0$$

The energy exchange by means of the promotion mode

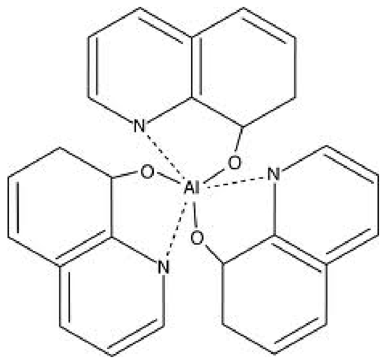


3. Charge carrier mobilities in OLED materials

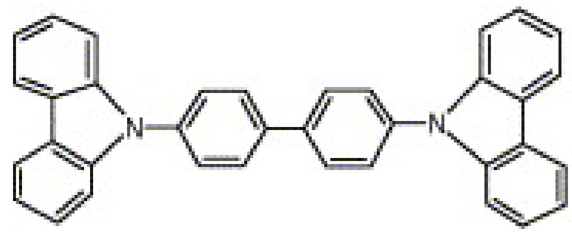
OLED = Organic Light Emitting Diode

Active ET centers of OLED systems are dimers $(M^{\pm})M$ appearing in applied electric fields

Typical monomer (M) molecules



AlQ_3



CBP

Dielectric permittivity for AlQ_3:

Static: $\varepsilon_s = 2.84$ (calculated)

or 3 ± 0.3 (experiment)*)

Optical: $2 < \varepsilon < 3$; Pekar factor < 0.1

<u>Conclusion</u>: the ET in OLED active centers is mainly associated with local molecular modes, rather than with medium polarization modes, as in usual ET theories

*) V. Ruhle et al, *JCTC* **7** (2011) 3335-3345

4. The ET without medium polarization

x – essentially quantum coordinate (two states 1 and 2)

$X(X_k)$ – local molecular modes (n or n' states: 1n and 2n')

$Q(Q_\nu)$ – medium modes with continuous frequency spectrum (the bath)

Both polarization and aqoustic phonon modes may be included in Q

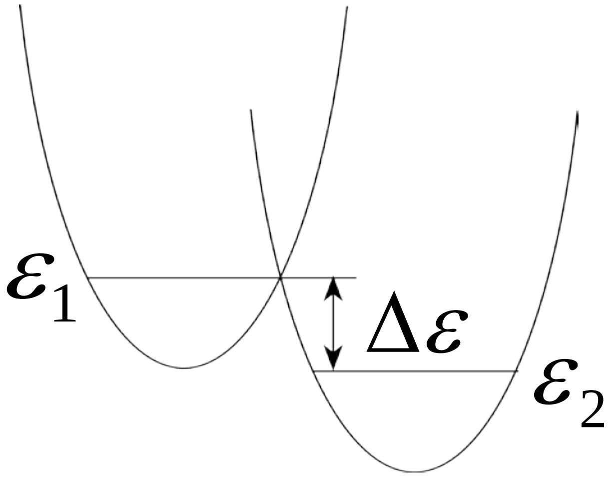
MLD – Marcus-Levich-Dogonadze (traditional ET)

DJ – Dogonadze-Jortner (including local modes)

The model	The interaction scheme	Comment
MLD (spin-boson)	x X Q	Strong x-Q, Q - polarization
DJ (generalized spin-boson)	x — X Q	Strong x-Q and x-X, Q – polarization. The same bath Q for all transitions 1n→2n'
Non-spin-boson (the present work)	x — X Q	Strong x-X and weak X-Q, Q – aqoustic phonons, X – dependent bath (XQ)

The connection to the continuum bath Q is obligatory in order to dissipate the energy misfit Δ of a ET reaction. This assures the convergence of rate integrals.

5. Fermi Golden Rate



P_{12} (transition probability per time unit)

$$P_{12} = \frac{2\pi}{\hbar} |V_{12}|^2 \delta(\varepsilon_1 - \varepsilon_2)$$

(purely incoherent transitions)

Spin-boson model: two levels (ε_1 and ε_2) in the continuum medium bath, which accepts the energy misfit $\Delta\varepsilon$

In the medium with continuum frequency spectrum

$$P_{12} = \frac{2\pi}{\hbar} |V_{12}|^2 \rho(\Delta\varepsilon)$$

distribution of the energy misfit

Coherent (resonance) transitions are neglected

6. Active ET local motions: Reorganization mode X (intramolecular) with frequency ω_0

Transfer integral:

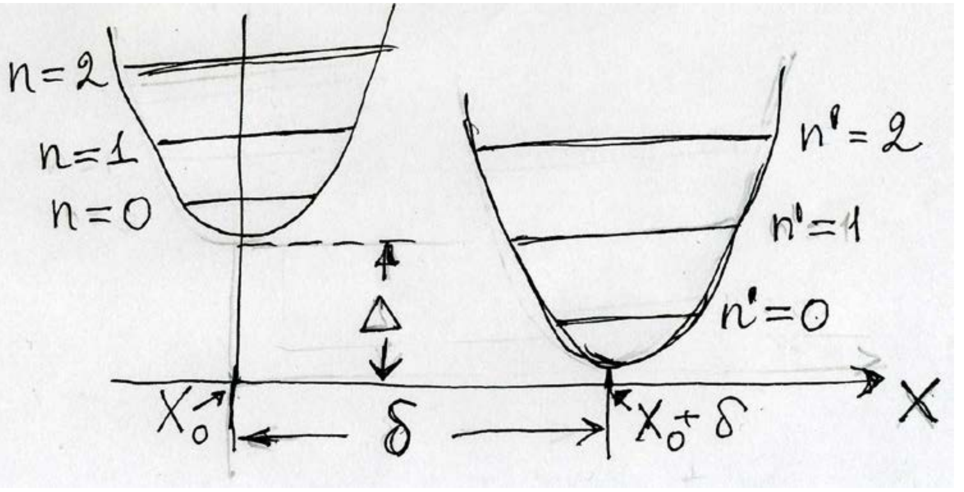
$$J_{nn'} = A_0 \left\langle \varphi_n(X) \middle| \hat{J}_X \middle| \varphi_n(X') \right\rangle \quad \hat{J}_X = \exp\left(-\delta \frac{d}{dX}\right) \quad \text{(shift operator)}$$

$\varphi_n(X)$ are oscillator functions:

$$J_{nn'} = A_0 \left\langle \varphi_n(X) \,|\, \varphi_n(X+\delta) \right\rangle$$

$$E_r = \frac{m\omega_0^2}{2}\delta^2$$

(reorganization energy)



A_0 and E_r (or δ) are the basic parameters

Marcus (1956; M)

Levich, Dogonadze (1959; LD)

MLD mechanism of ET

δ is the shift of the equilibrium position X_0

Δ is the reaction energy change

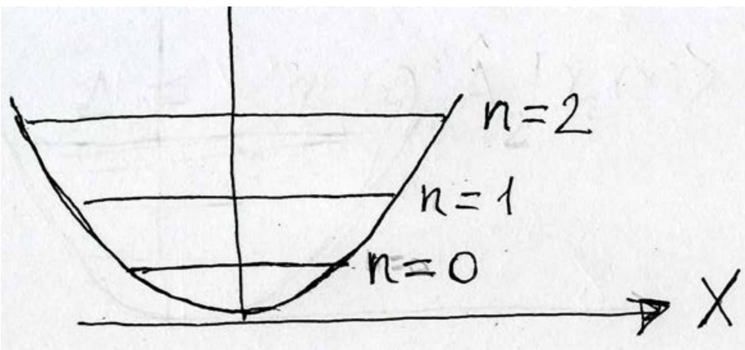
7. Active ET local motions: promotion mode X (intermolecular) with frequency ω_0

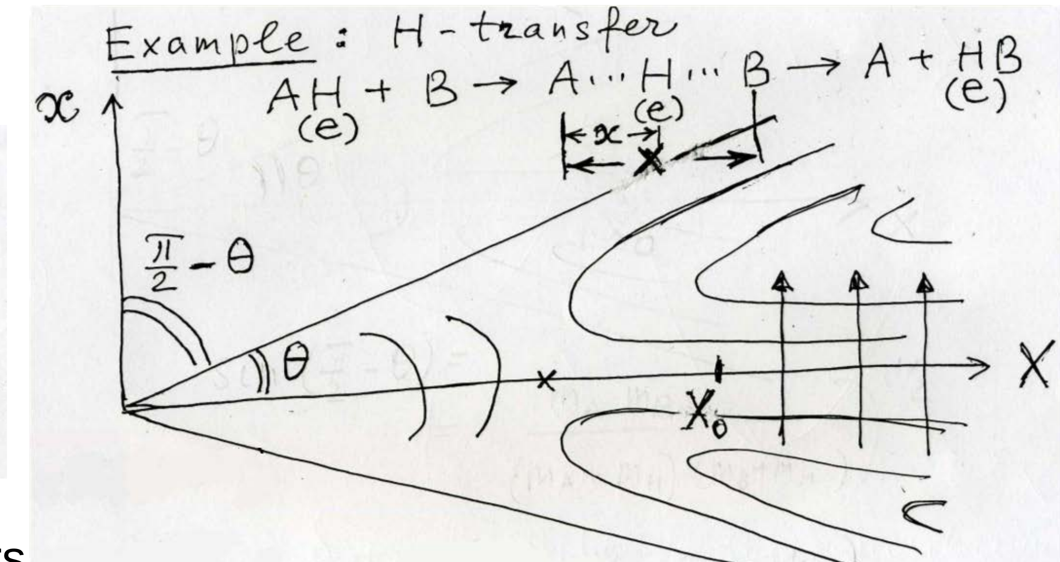
Transfer integral: $J_{nn'} = \left\langle \chi_1(x)\varphi_n(X) \middle| \hat{J} \middle| \chi_2(x)\varphi_{n'}(X) \right\rangle = A_0 \left\langle \varphi_n(X) \middle| \hat{J}_X \middle| \varphi_{n'}(X) \right\rangle$

$\chi_i(X)$ are electron (or H) functions

$$\hat{J}_X = \exp\left(-\mu\left(X - X_0\right) - \nu\left(X - X_0\right)^2\right)$$

$\varphi_n(X)$ are oscillator functions





A_0, μ and ν are the basic parameters

Miller, Abrahams (1960; MA→ET)

Trakhtenberg, Klochikhin, Pshezhetski (1982; T → H transfer)

MAT mechanism of ET or HT

$$\sin\left(\frac{\pi}{2} - \theta\right) = \left[\frac{m_A m_B}{\left(m_A + m_H\right)\left(m_B + m_H\right)}\right]^{1/2}$$

$$\theta = 8^0 \quad \text{(H transfer)}$$

$$\theta = 0.6^0 \quad (ET)$$

8. The ET kinetics (Levich, Dogonadze, 1959)

$$K(T) = \frac{2\pi}{\hbar}\frac{C(T)}{Z(T)} \quad (1)$$

Eq. (1) is derived from the Fermi “Golden Rule”

The present work follows our approach suggested in 2006:

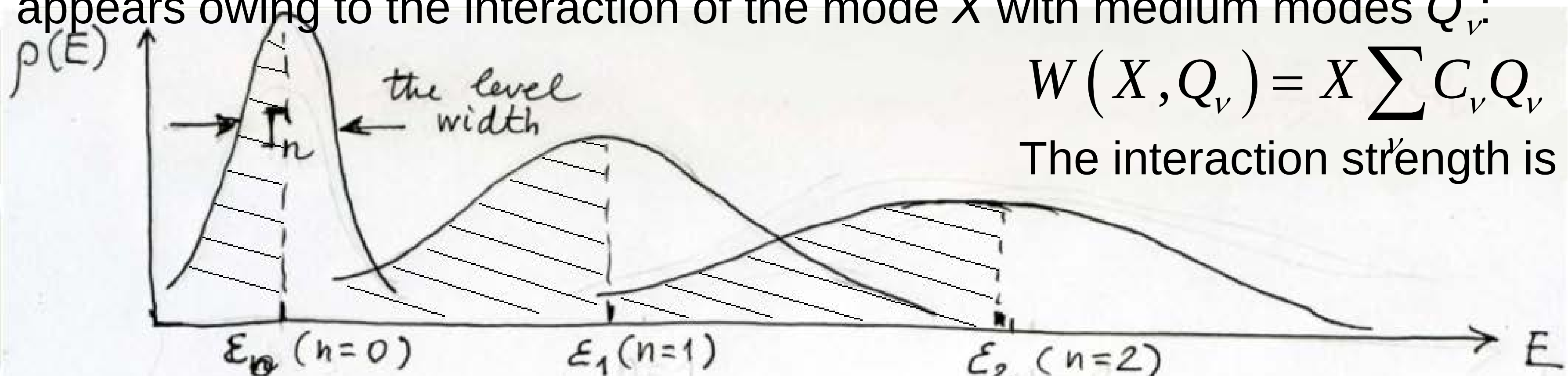
$$C(T) = \sum_{n,n'}\int_0^\infty dE \exp\left(-\frac{E}{k_B T}\right)\left|J_{nn'}^2\right|\rho_n(E)\rho_{n'}(E) \rightarrow \text{the reaction probability flux}$$

$$Z(T) = \sum_{n}\int_0^\infty dE \exp\left(-\frac{E}{k_B T}\right)\rho_n(E) \rightarrow \text{the partition function}$$

The energy distributions $\rho_n(E)$ are the basic quantities. The level broadening appears owing to the interaction of the mode *X* with medium modes Q_ν:

$$W\left(X, Q_\nu\right) = X\sum_\nu C_\nu Q_\nu$$

The interaction strength is g



$$\varepsilon_n = \left(n + \frac{1}{2}\right)\hbar\omega_0; \qquad \Gamma_n = \left[(2n+1)\coth\frac{\hbar\omega_0}{k_B T} - 1\right] \text{g}$$

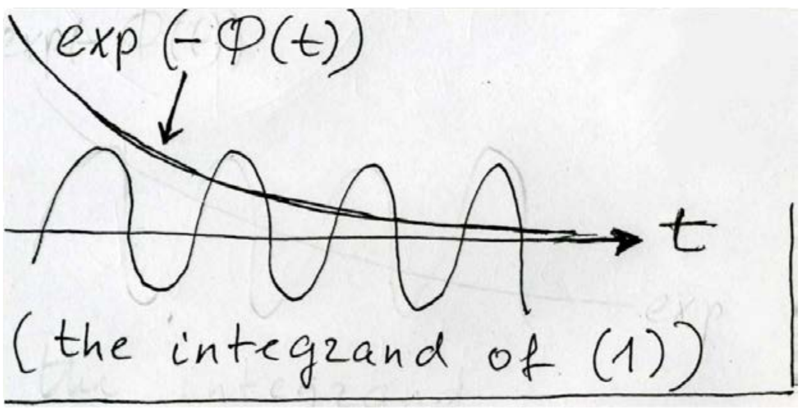
n-dependent continuous frequency spectrum destroys the spin-boson model

9. ET dynamics/kinetics

$$K(T) = const \int_{-\infty}^{+\infty} \cos\left(\frac{\Delta}{\hbar\omega_0} t\right) \exp\left(-\Phi(t)\right) dt \quad (1)$$

Rate constant is determined by the dissipation of the energy misfit Δ

ω_0 *is the frequency;* Δ *is the reaction energy change*



Φ(t) is extremely complicated in the full theory (LD, 1959; the reorganization mode *X* with frequency ω_0)

Marcus (1956; the reorganization mode *X*):

$$K(T) = \frac{A_0^2}{\hbar}\sqrt{\frac{\pi}{E_r k_B T}} \times \exp\left[-\frac{(\Delta + E_r)^2}{4k_B T E_r}\right] \quad (2)$$

Invoking the promotion mode X is quite unusual in the ET theory (i.e. the MA mechanism is usually disregarded)

Eq. (2) is the asymptotic limit of (1), purely classical, i.e. ħ ω_0 /kT<<1

10. The spectral functions ρ_n(t) and f(t)

$$\rho_n(E) = \rho_n(\omega) = \int_{-\infty}^{+\infty} \rho_n(t)\exp(i\omega t)dt; \quad \omega = \frac{E-\varepsilon_n}{\hbar\omega_0}$$

(the energy level distribution)

$$\rho_n(t) = \frac{1}{2\pi}\exp\left[-\frac{\Gamma_n}{2\hbar\omega_0}f(t)\right] \quad \text{(the spectral function)} \qquad (1)$$

$$f(t) = |t| + \frac{1}{b}\left(e^{-b|t|}-1\right) \quad \text{(Kubo, Toda, Hashitsume, 1978, 1986)}$$

$$\Gamma_n = \left[(2n+1)\coth\frac{\hbar\omega_0}{2k_BT}-1\right]\mathrm{g} \quad \tilde{\varepsilon}_n = \left(n+\frac{1}{2}\right)\hbar\omega_0 - i\frac{\Gamma_n}{2} \qquad (2)$$

Eq. (2) is derived based on the quantum relaxation equation (Bloch, Redfield); g is the strength of *X*/medium interaction:

$$W\left(X,Q_\nu\right) = X\sum_\nu C_\nu Q_\nu = XQ, \quad Q = \sum_\nu C_\nu Q_\nu \qquad (3)$$

*Parameters b (Eq. (1)) and g (Eq. (2)) can be extracted from the correlation function C(t)=<Q(t=0)*Q(t)>, where Q(t) Eq. (3)) is the collective medium coordinate (the medium induced random force).*

11. The basic parameters

ω_0 – the frequency of the local mode *X*

J_0 – the transfer integral

E_r – the reorganization energy $\dfrac{E_r}{\hbar\omega_0}$

$\Delta = E_2 - E_1$ – the reaction energy change $\left(\dfrac{\Delta}{\hbar\omega_0}\right)$

} for the reorganization mode *X*

μ, ν – the parameters of the transfer integral $J = J_0 \exp(-\mu X - \nu X^2)$

$\Delta = E_2 - E_1$ – the reaction energy change $\left(\dfrac{\Delta}{\hbar\omega_0}\right)$

} for the promotion mode *X*

g-the strength of the mode/medium interaction

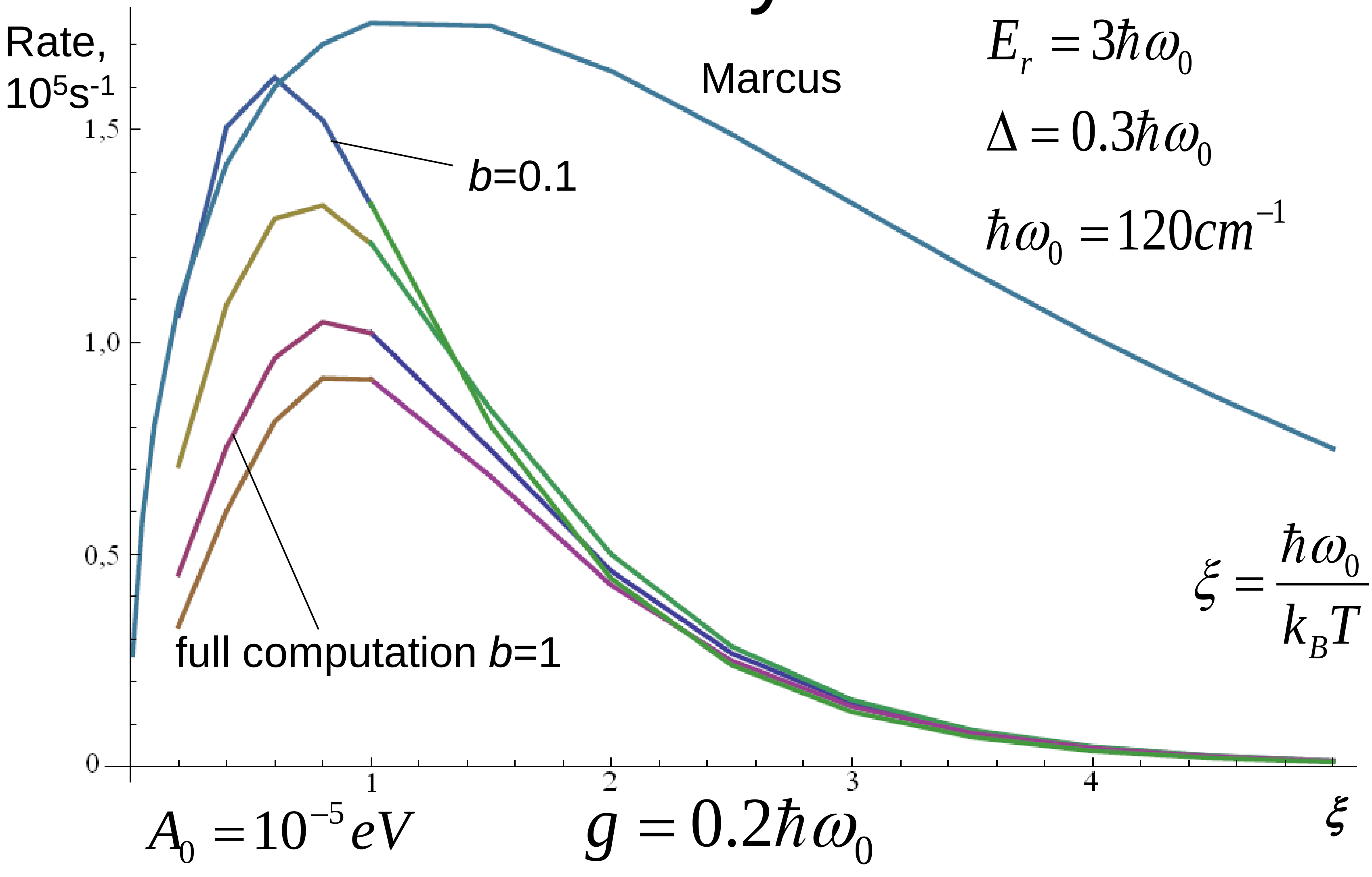
b – the parameter of Kubo function $f(t) = |t| + \dfrac{1}{b}\left(\exp(-b|t|) - 1\right)$

} specific for the present approach

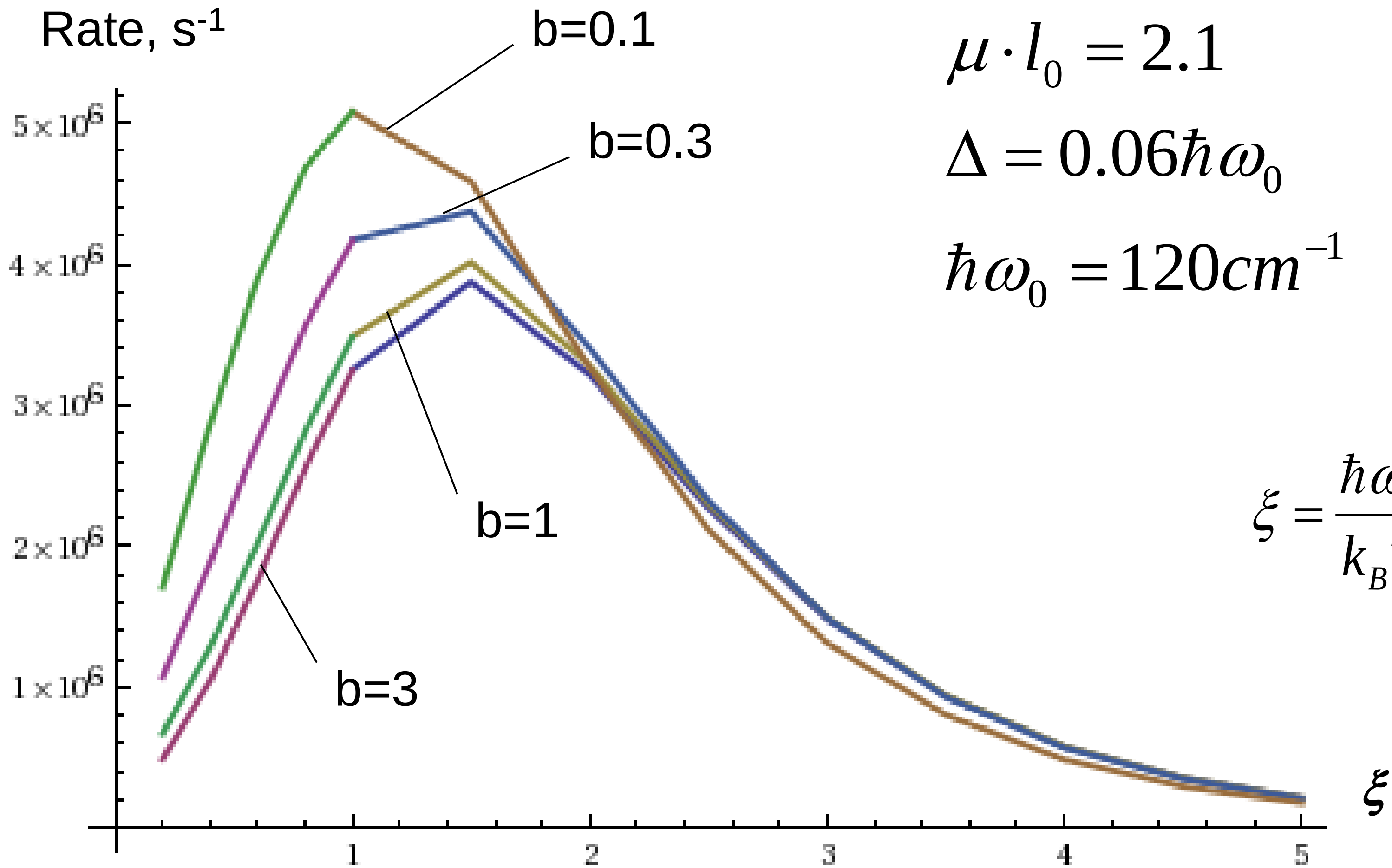
The important parameter $\xi = \dfrac{\hbar\omega_0}{k_B T}$

determines the kinetic regime in the whole temperature range

12. The ET kinetics in typical OLED systems



13. The ET kinetics for promotion mode



$$\mu \cdot l_0 = 2.1$$

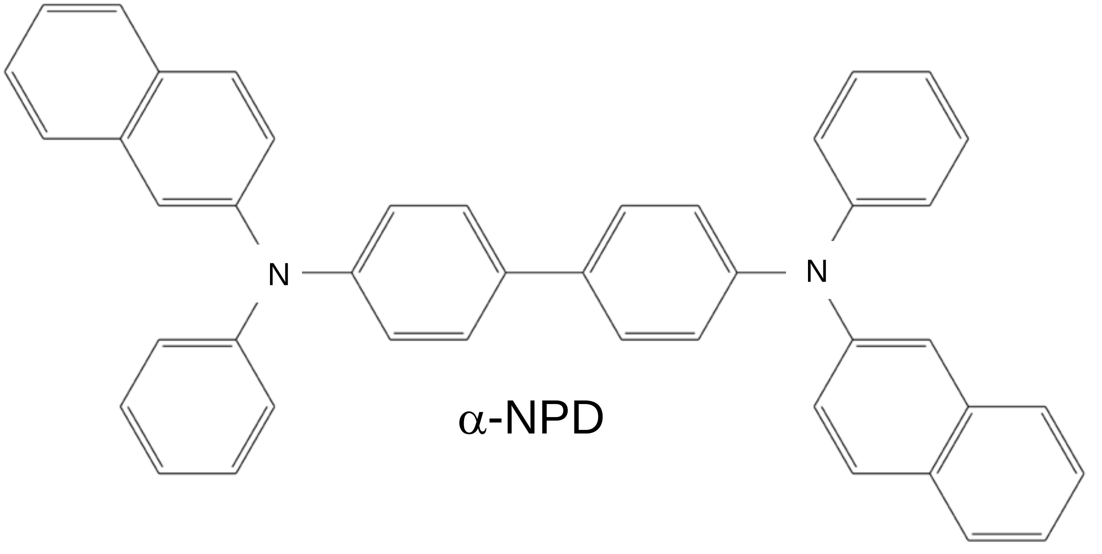
$$\Delta = 0.06\hbar\omega_0$$

$$\hbar\omega_0 = 120 cm^{-1}$$

$$\xi = \frac{\hbar\omega_0}{k_B T}$$

$$A_0 = 10^{-5} eV \qquad g = 0.2\hbar\omega_0$$

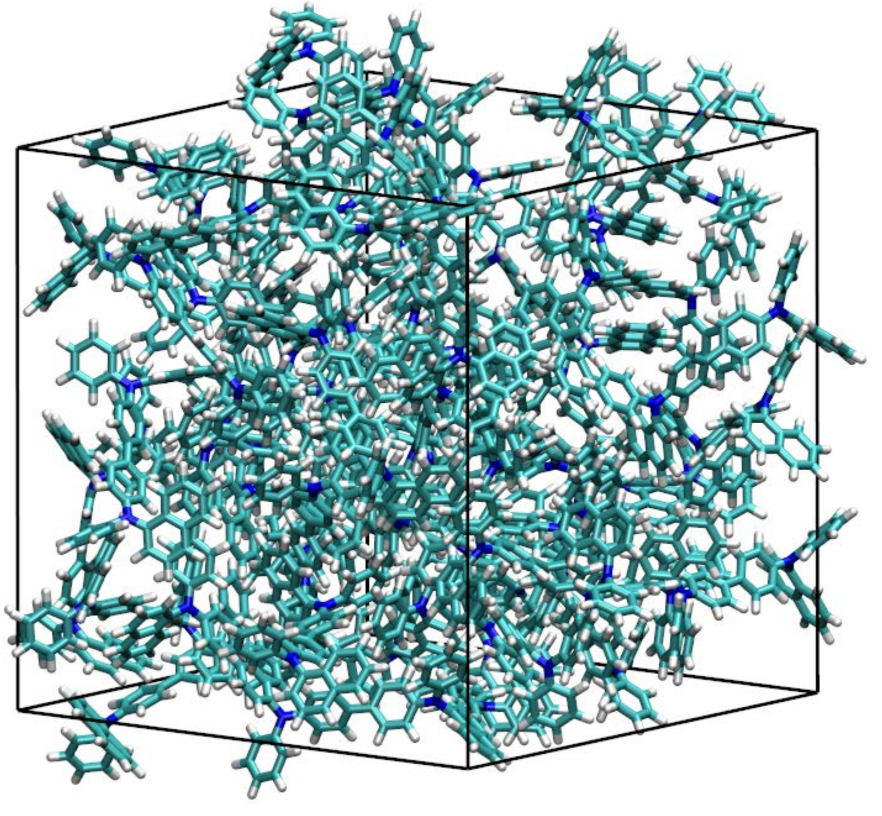
14. The conduction material



α-NPD

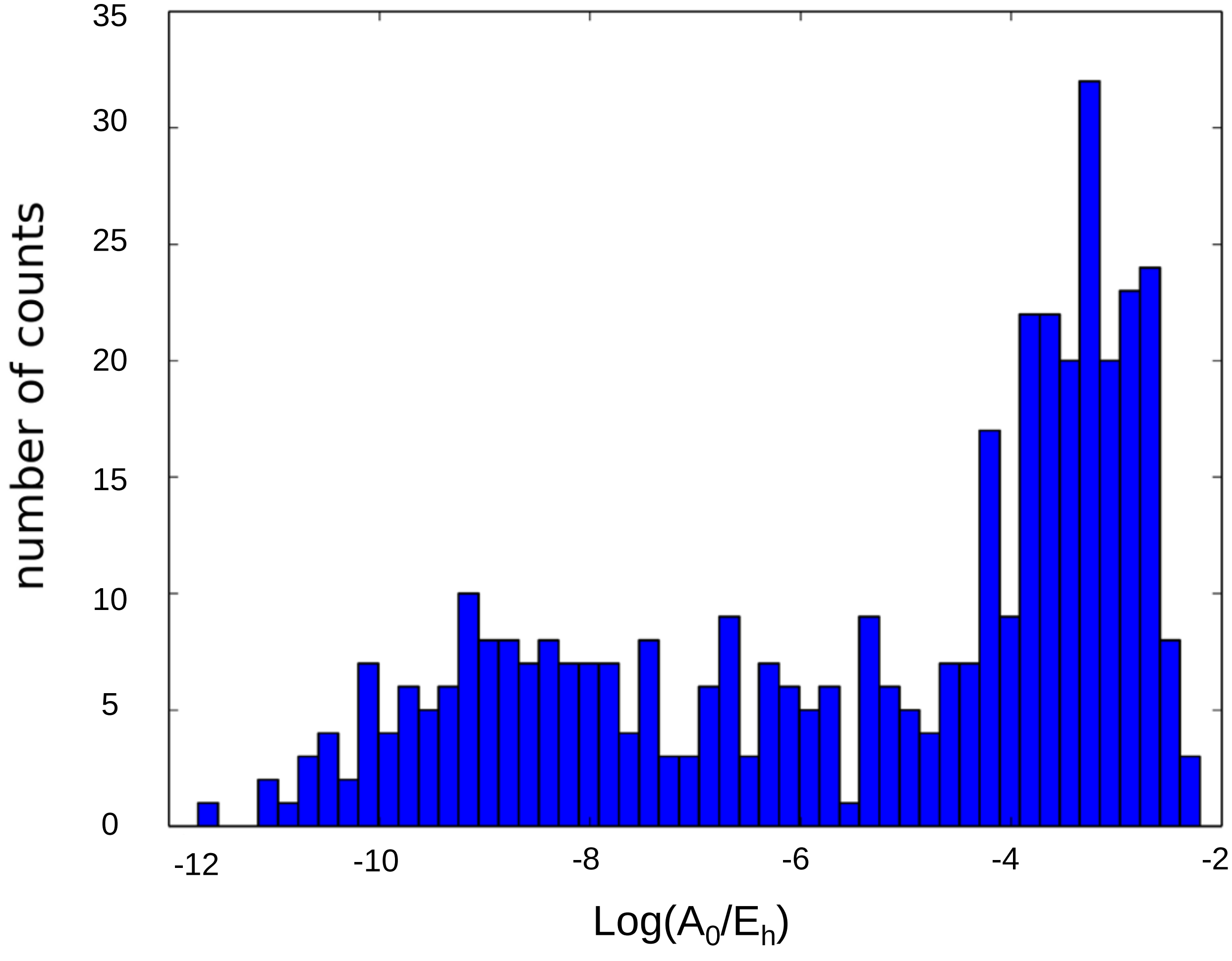
N,N – di[1-heptaphenyl – N,N-diphenyl] – 1,1 biphenyl – 4,4 diamine

15. The MD simulation of amorphous α-NPD material.



the MD cell contains 50 α-NPD molecules

16. The distribution of transfer integrals A_0



17. The computations for eight α-NPD dimers

№	A_0, **10^{-2} eV**	μ, **nm^{-1}**	ω_0, **cm^{-1}**	b/ω_0	g/ω_0	$\langle x^2 \rangle$, **nm^2**	**Δ, eV**	$\log(K_{ij})$, **s^{-1}**
1	0.85	20.1	155	47.8	1.12	0.021	-0.53	12.66
2	1.51	17.0	218	12.2	0.86	0.020	-0.22	13.33
3	1.09	16.0	183	17.6	1.04	0.023	-0.08	12.75
4	2.68	28.1	190	37.6	0.75	0.019	-0.40	15.51
5	2.29	3.4	187	12.0	1.01	0.019	-0.76	12.21
6	2.55	13.6	236	11.2	0.80	0.019	-0.24	13.34
7	0.93	23.2	149	22.3	1.15	0.034	-0.18	14.24
8	1.94	34.6	158	20.8	0.92	0.022	-1.24	16.50

A_0: transfer integrals (QC)   Δ: the energy misfit (QC) K_{ij}: the calculated rate constant

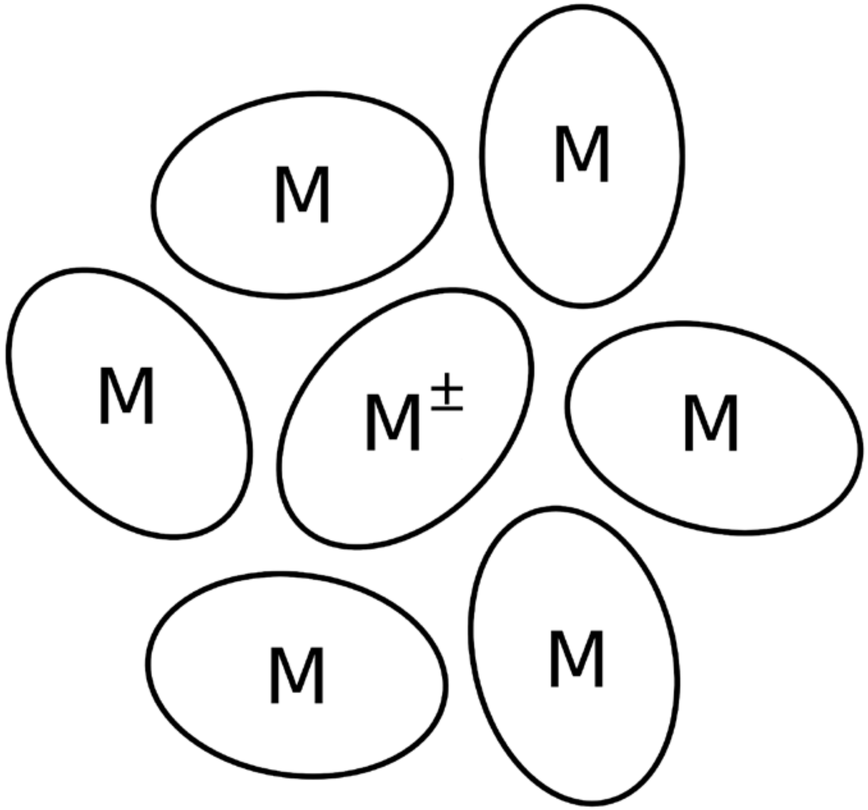
$$\mu:\ A_0(X) = A_0 \exp\left[-\mu\left(X - X_0\right)\right]$$

ω_0: the frequency of promotion mode

b,g: the relaxation parameters

MD simulation of the velocity correlation function $\left\langle \dot{X}(t=0) \cdot \dot{X}(t) \right\rangle$

The ET scheme. The reaction center



$$M^+M \longrightarrow MM^+ + \Delta$$

$$K(T) << \begin{pmatrix} \omega_{ext} \\ \omega_{rel} \end{pmatrix} << \omega_{\text{int}} \approx \omega_0$$

The energy exchange by means of the promotion mode