

The microscopic model of the electron transfer in disordered solid matrices

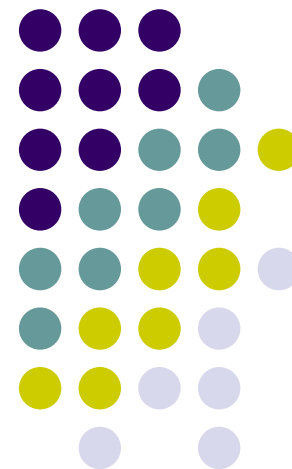
M. V. Basilevsky

A. V. Odinokov

Photochemistry Center, RAS

S. V. Titov

Karpov Institute of Physical Chemistry



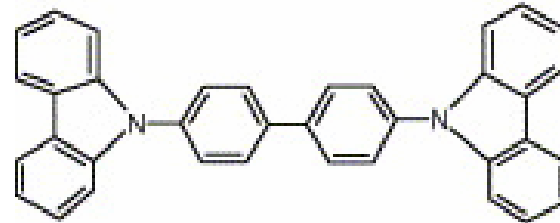
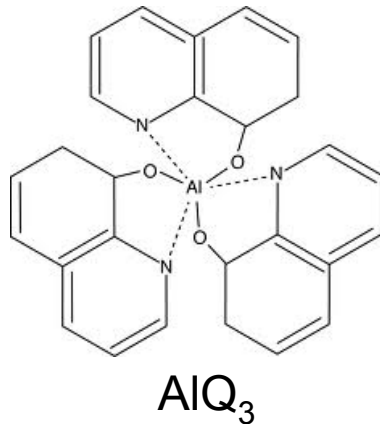
1. Charge carrier mobilities in OLED materials



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



Dielectric permittivity for AlQ₃:

Static: $\epsilon_s = 2.84$ (calculated)

or 3 ± 0.3 (experiment)*)

Optical: $2 < \epsilon < 3$

Conclusion: 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

2. 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
acoustic phonon modes may
be included

MLD – Marcus-Levich-Dogonadze (traditional ET)

DJ – Dogonadze-Jortner (including local modes)

The model	The interaction scheme	Comment
MLD (spin-boson)	$\begin{array}{c} x \quad X \\ \quad \diagdown \quad / \\ \quad \quad Q \end{array}$	Strong x-Q, Q - polarization
DJ (generalized spin-boson)	$\begin{array}{c} x \text{---} X \\ \quad \diagdown \quad / \\ \quad \quad Q \end{array}$	Strong x-Q and x-X, Q – polarization. The same bath Q for all transitions 1n→2n'
Non-spin-boson (the present work)	$\begin{array}{c} x \text{---} X \\ \quad \quad \diagdown \quad / \\ \quad \quad \quad Q \end{array}$	Strong x-X and weak X-Q, Q – acoustic phonons, n - dependent

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.

3. Active ET local motions: Reorganization mode X (intramolecular)



Transfer
integral:

$$J_{nn'} = J_0 \langle \varphi_n(X) | \hat{J}_X | \varphi_{n'}(X') \rangle \quad \hat{J}_X = \exp\left(-\delta \frac{d}{dX}\right) \quad (\text{shift operator})$$

$\varphi_n(X)$ are oscillator functions: $J_{nn'} = J_0 \langle \varphi_n(X) | \varphi_{n'}(X + \delta) \rangle$

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

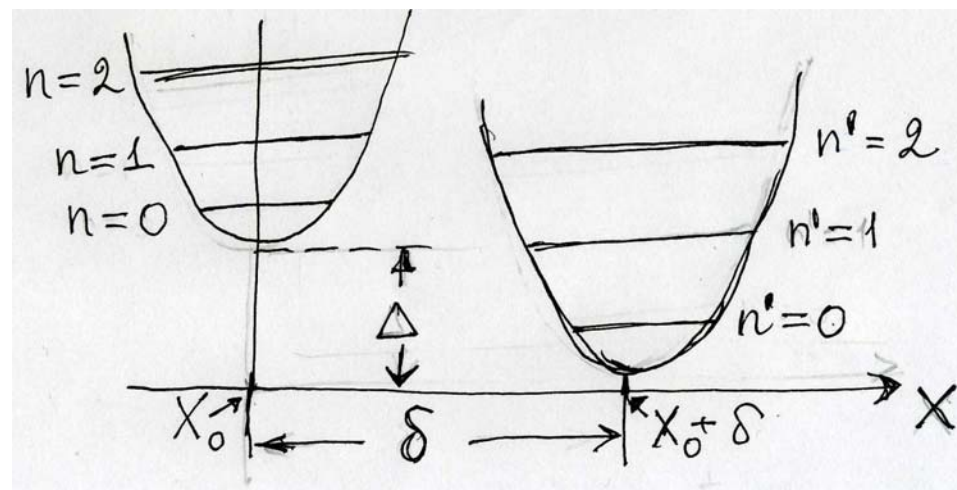
(reorganization energy)

J_0 and E_r (or δ) are
the basic parameters

Marcus (1956; M)

Levich, Dogonadze (1959; LD)

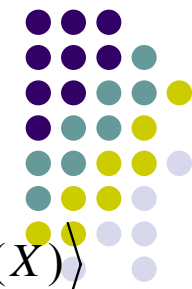
MLD mechanism of ET



δ is the shift of the equilibrium position X_0

Δ is the reaction energy change

4. Active ET local motions: promotion mode X (intermolecular)



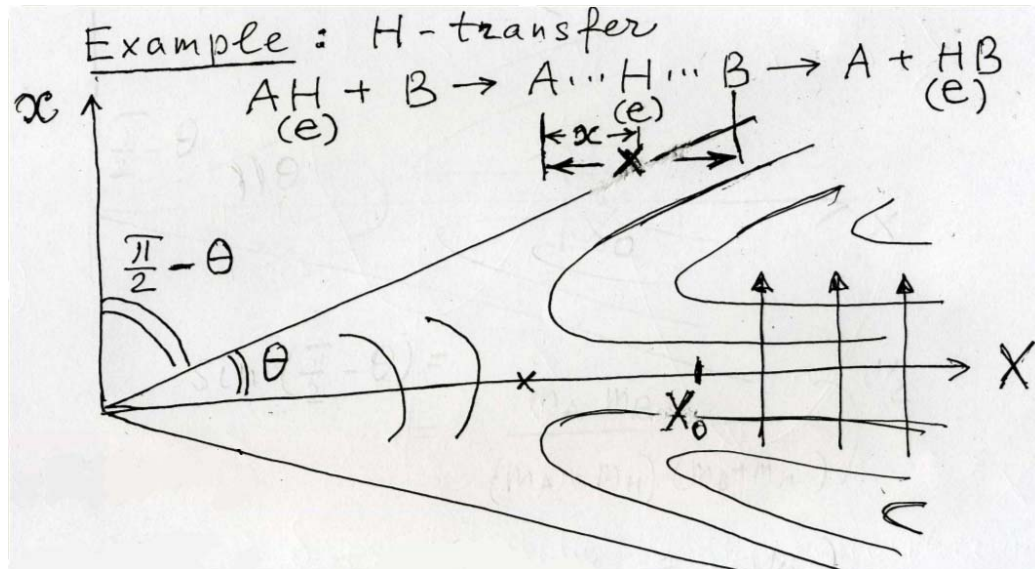
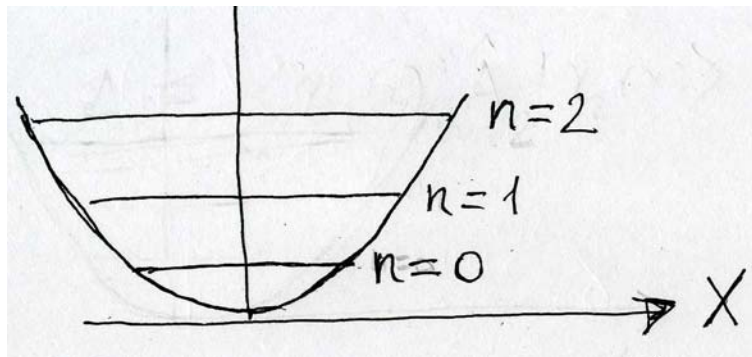
Transfer integral:

$$J_{mn'} = \langle \chi_1(x) \varphi_n(X) | \hat{J} | \chi_2(x) \varphi_{n'}(X) \rangle = J_0 \langle \varphi_n(X) | \hat{J}_X | \varphi_{n'}(X) \rangle$$

(x) are electron (or H) functions

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

$\varphi_n(X)$ are oscillator functions



J_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

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

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

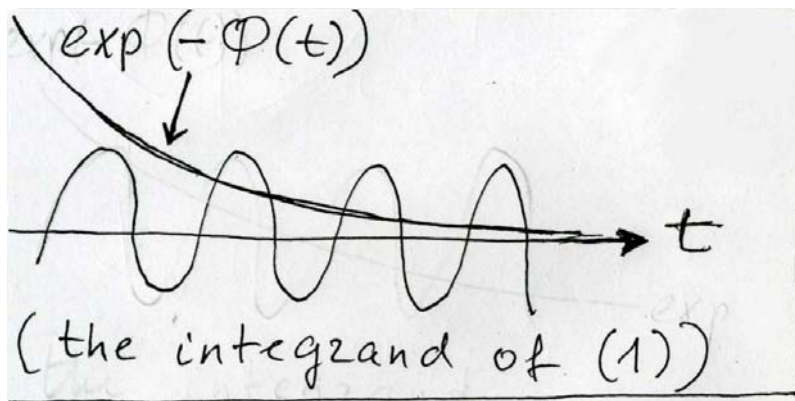
$$\theta = 0.6^\circ \quad (\text{ET})$$

5. ET dynamics/kinetics



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

Rate constant is determined by the dissipation of the energy misfit Δ
 ω_0 is the frequency; $\Phi(t)$ is the reaction energy change



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

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

Marcus (1956; the reorganization mode X):

$$K(T) = \frac{J_0^2}{E_r k_B T} \sqrt{\frac{\pi}{E_r k_B T}} \times \exp\left[-\frac{(\Delta + E_r)^2}{4k_B T E_r}\right] \quad (2)$$

Eq. (2) is the asymptotic limit of (1), purely classical, i.e. $\hbar \omega_0 / k_B T \ll 1$

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



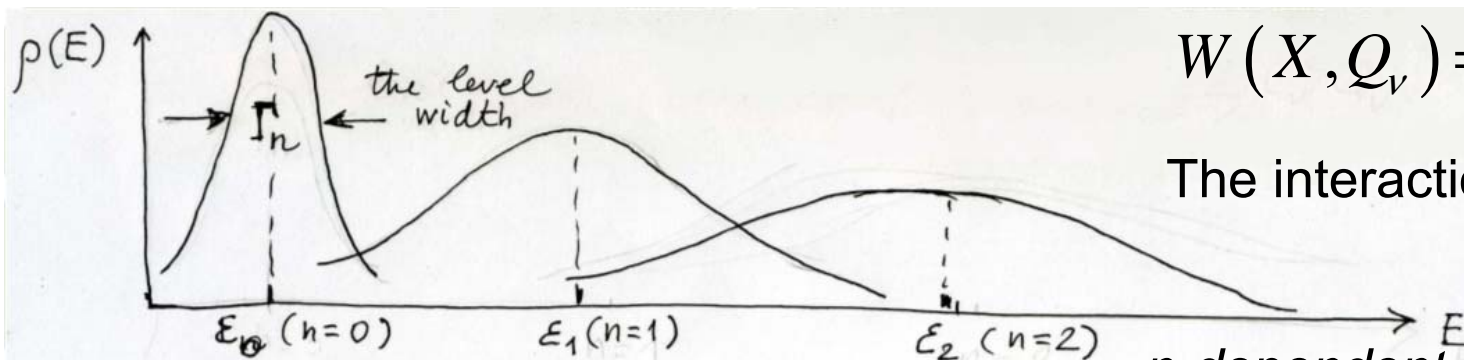
$$K(T) = \frac{2\pi C(T)}{Z(T)} \quad (1) \quad \text{Eq. (1) is derived from the Fermi "Golden Rule"}$$

The present work follows our approach suggested in 2006:

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

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

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 :



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

The interaction strength is

$$\epsilon_n = \left(n + \frac{1}{2}\right) \omega_0; \quad \Gamma_n = \left[(2n + 1) \coth \frac{\omega_0}{k_B T} - 1 \right] \gamma$$

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

7. The spectral functions $\rho_n(t)$ and $f(t)$



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

(the energy level distribution)

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

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

$$\Gamma_n = \left[(2n+1) \coth \frac{\omega_0}{2k_B T} - 1 \right] \gamma; \quad \varepsilon_n = \left(n + \frac{1}{2} \right) \omega_0 - i \frac{\Gamma_n}{2} \quad (2)$$

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

$$W(X, Q_v) = X \sum_v C_v Q_v = XQ, \quad Q = \sum_v C_v Q_v \quad (3)$$

Parameters b (Eq. (1)) and γ (Eq. (2)) can be extracted from the correlation function $C(t) = \langle Q(t=0)^* Q(t) \rangle$, where $Q(t)$ (Eq. (3)) is the collective medium coordinate (the medium induced random force).

8. The basic parameters



ω_0 – the frequency of the local mode X

J_0 – the transfer integral

E_r – the reorganization energy $\frac{E_r}{\omega_0}$
 $= E_2 - E_1$ – the reaction energy change $\left(\frac{\Delta}{\omega_0}\right)$ } for the reorganization mode X

γ – the parameters of the transfer integral $J = J_0 \exp(-\gamma X^2)$
 $= E_2 - E_1$ – the reaction energy change $\left(\frac{\Delta}{\omega_0}\right)$ } for the promotion mode X

b – the strength of the mode/medium interaction
 b – the parameter of Kubo function $f(t) = |t| + \frac{1}{b}(\exp(-b|t|) - 1)$ } specific for the present approach

The important parameter $\xi = \frac{\omega_0}{k_B T}$
 determines the kinetic regime in the whole temperature range

9. What is the target of computation



$$K(T) = \frac{2\pi C(T)}{Z(T)} \quad \left\{ \begin{array}{l} \leftarrow \text{the reaction probability flux} \\ \leftarrow \text{the partition function} \end{array} \right.$$

$$C(T) = \frac{J_0^2}{2\pi} \exp\left(-\frac{\Delta}{2k_B T}\right) \times \int_{-\infty}^{+\infty} \frac{dv}{\omega_0} \exp\left(i\frac{\Delta}{\omega_0}v\right) \times \exp\left[\frac{\gamma}{\omega_0} \operatorname{Re} f(\bar{z})\right] \times I(\bar{z}, \bar{z}')$$

$$\bar{z} = -\frac{i\xi}{2} + v; \quad \bar{z}' = -\frac{i\xi}{2} - v; \quad \xi = \frac{\omega_0}{k_B T}$$

$I(z, z')$ is the two-point integral kernel (the known analytical expression). It is specific for reorganization and promotion modes. Includes the Kubo function $f(z)$.

$$Z(T) = \exp\left(\frac{\gamma}{2\omega_0} f(z)\right) / 2 \sinh\left\{\frac{1}{2}\left[iz + \frac{\gamma}{\omega_0}\left(\coth\frac{\xi}{2}\right)f(z)\right]\right\}; \quad z = \frac{1}{i}\xi$$

For the Kubo function the analytical continuation in the complex time plane $z = v - iu$ is required:

$$\rho(z) = \frac{1}{\pi i} \int_{-\infty}^{+\infty} \frac{\rho_1(v)}{v - z} dv, \quad \text{where} \quad \rho_1(v) = \exp\left[-\frac{\gamma}{2\omega_0} f(v)\right]$$

$$f(v) = |v| + \frac{1}{b} \left[\exp(-b|v|) - 1 \right] \quad (\text{the Kubo function})$$



10. Reminder

$$\xi = \frac{\omega_0}{k_B T} = \frac{\omega_0}{\omega_T}; \quad \omega_T = \frac{k_B T}{\hbar}$$

This important parameter essentially determines the kinetic regime, in which the ET process proceeds

$\xi \ll 1$ for a classical regime

$\xi \gg 1$ for a quantum regime

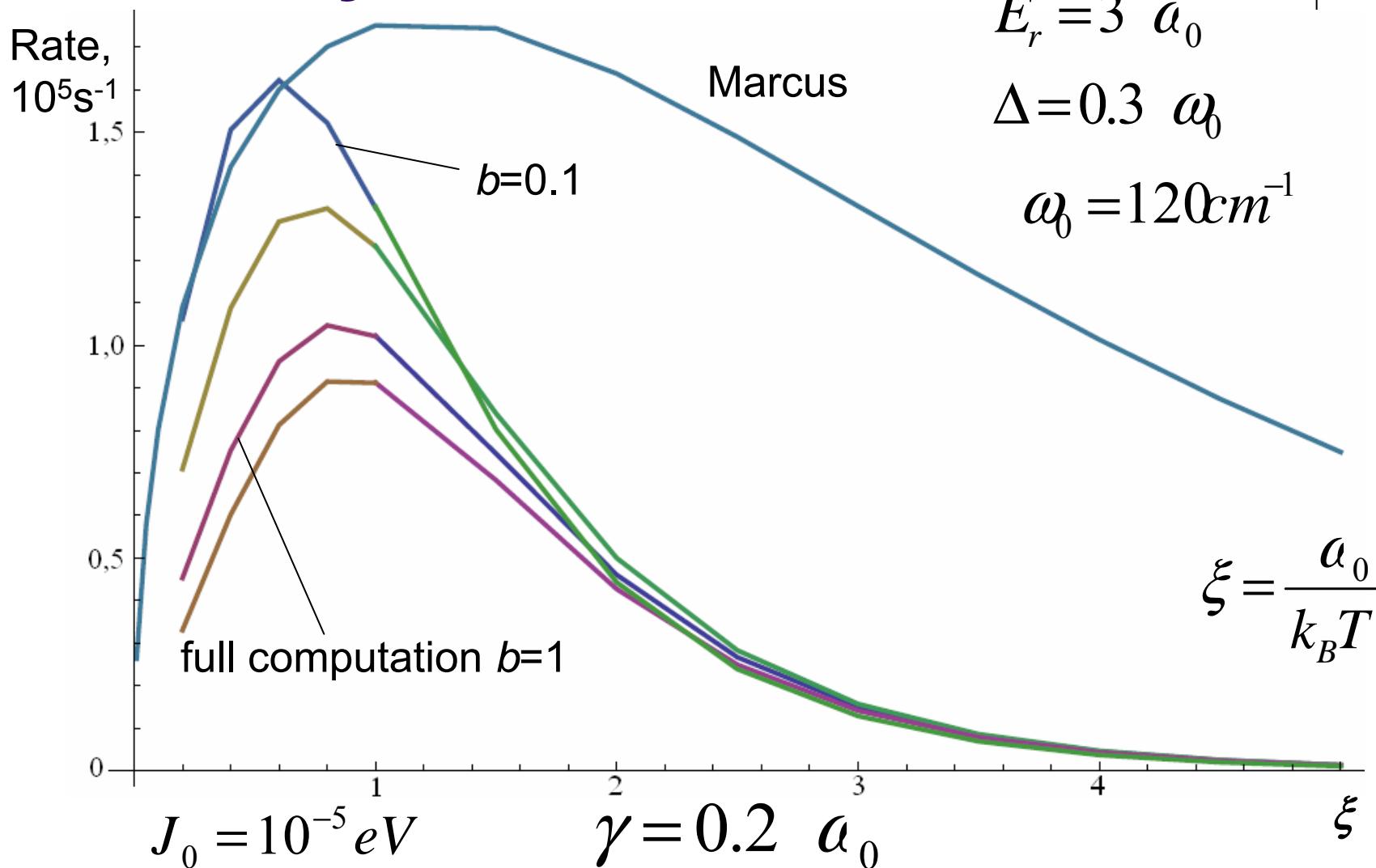
So, $\xi < 1$ for:

ω_0, cm^{-1} : 400 200 130 100 65 30 10

T, K : > 600 > 300 > 200 > 150 > 100 > 45 > 15

The present code covers this range

11. The ET kinetics in typical OLED systems



12. The ET kinetics for typical liquid phase polar environment

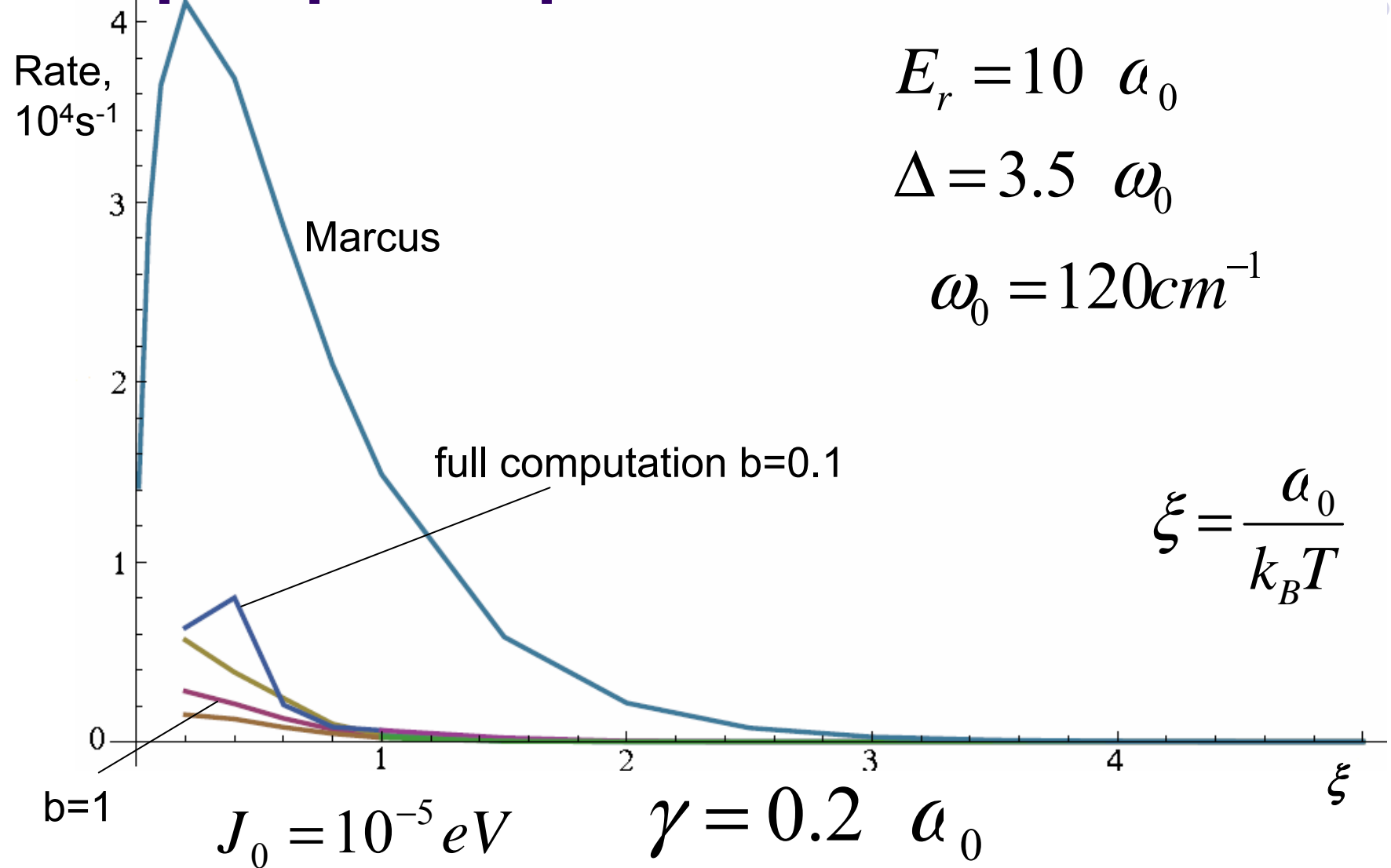


$$E_r = 10 a_0$$

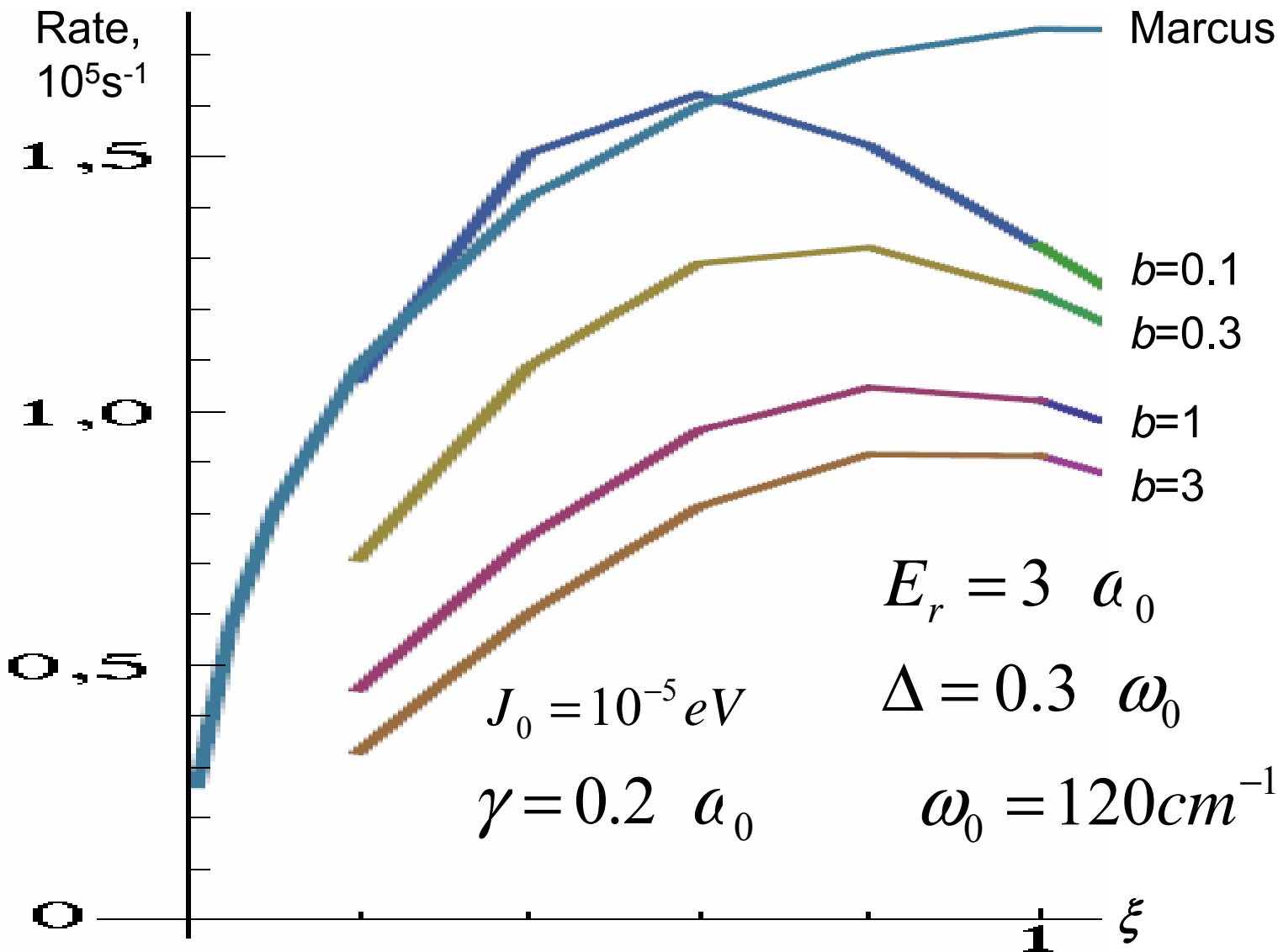
$$\Delta = 3.5 \omega_0$$

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

$$\xi = \frac{a_0}{k_B T}$$



13. The ET kinetics in the high-temperature regime: $\xi < 1$. Typical OLED systems



$$\xi = \frac{a_0}{k_B T}$$

14. The ET kinetics for promotion mode

