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WORKSHOP ON "NON-LINEAR ELECTROMAGNETIC INTERACTIONS IN SEMICONDUCTORS"

1 - 10 AUGUST 1994

"Excitons and Optical Nonlinearities in Organic Quantum Wells and Superlattices"

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These are preliminary lecture notes, intended only for distribution to participants

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EXCITONS AND OPTICAL NONLINEARITIES IN ORGANIC QUANTUM WELLS AND SUPERLATTICES

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1.INTRODUCTION : FRENKEL-WANNIER- MOTT

2.EXCITONS IN ORGANICS: FRENKEL AND CHARGE TRANSFER EXCITONS

3.ORGANIC CRYSTALLINE NANOSTRUCTURES-NEW MATERIALS FOR SCIENCE AND APPLICATIONS.
RECENT PROGRESS IN GROWTH AND CHARACTERIZATION.

4.FIRST EXPERIMENTAL OBSERVATIONS OF EXCITONS IN ORGANIC MULTILAYER STRUCTURES AND "SMALL RADIUS" MODEL.

5.THE CREATION OF ORGANIC MULTILAYER NANOSTRUCTURES OPENS A NEW FIELD OF RESONANT MOLECULAR OPTICS:

A. FERMI RESONANCE INTERFACE MODES AND BISTABILITY AND MULTISTABILITY IN THE ENERGY TRANSMISSION THROUGH THE INTERFACE.

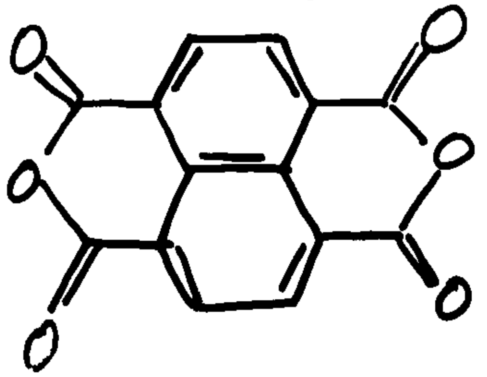
B. HYBRID EXCITON STATES AT ORGANIC-INORGANIC INTERFACE.

6.ELECTRONIC PHASE TRANSITION IN THE SYSTEM OF INTERFACE CHARGE TRANSFER EXCITONS AT HIGH CONCENTRATION.

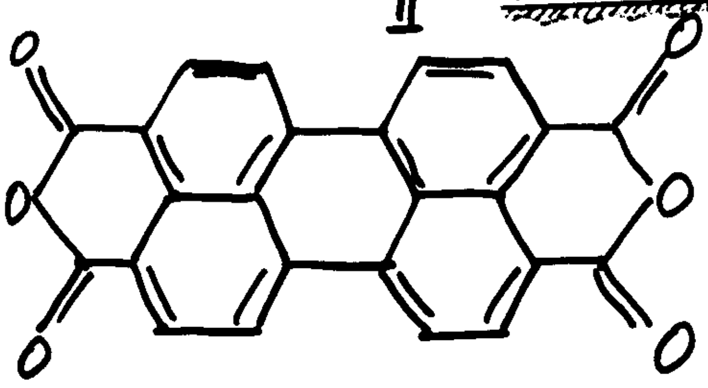
Organic superlattices

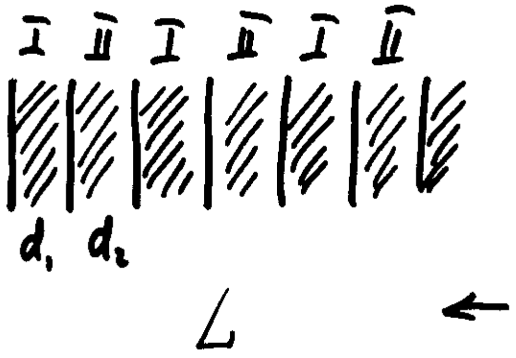
F. F. So et al. Appl. Phys. Lett. 56 (7), 1990

I NTCDA



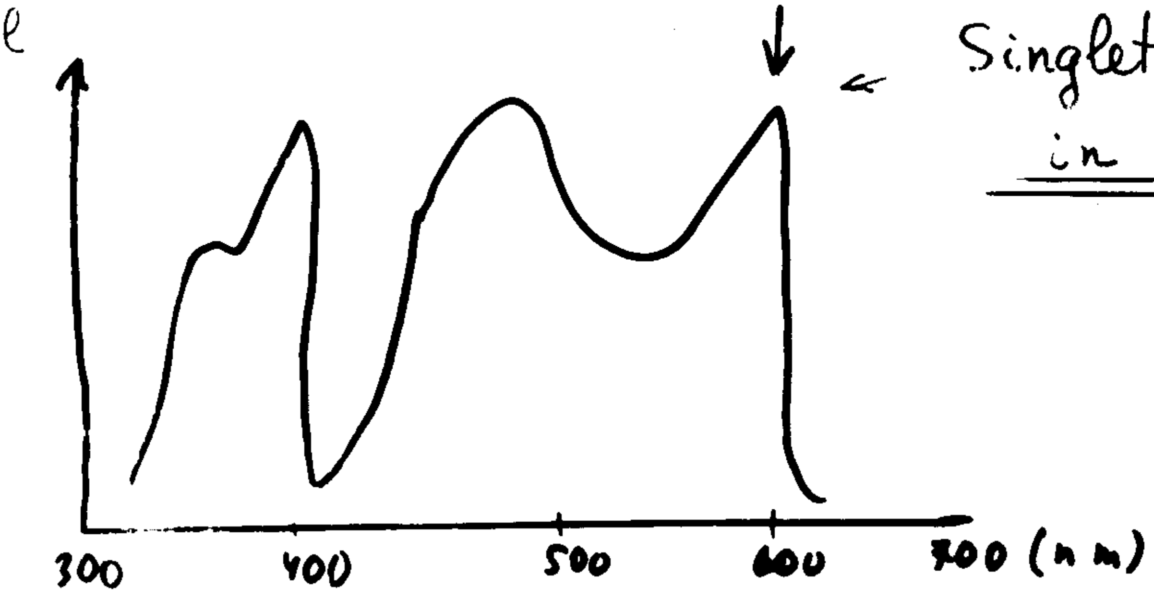
II PTCDA





$d_1 = d_2 = 10Å — 200Å$

$L \sim 1500Å$



Singlet exciton in PTCDA

S. Forrest (1990, 91), Armstrong R.S. (Tuson)

-os- Ang.

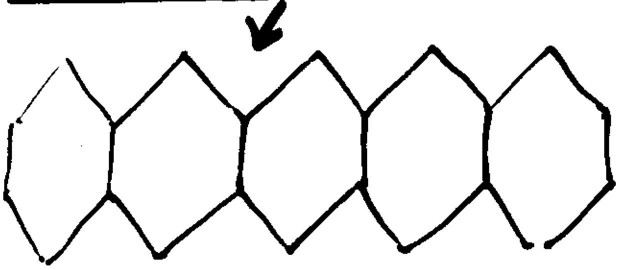
1992

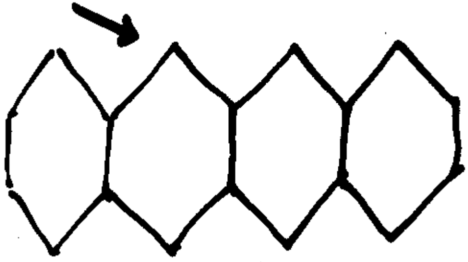
Karl N. (stuttgart)

H. Sakaki (Tokyo) 1993

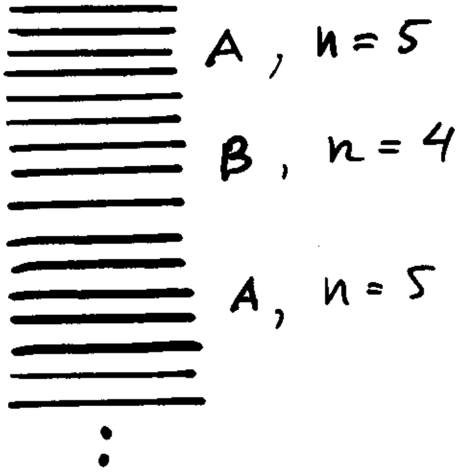
Maruyama Y. (Okazaki)

Pentacene / Tetracene SL


A


B

A(5)/B(4)



P(n)/T(n), for

n ≥ 3 → Superlattices.

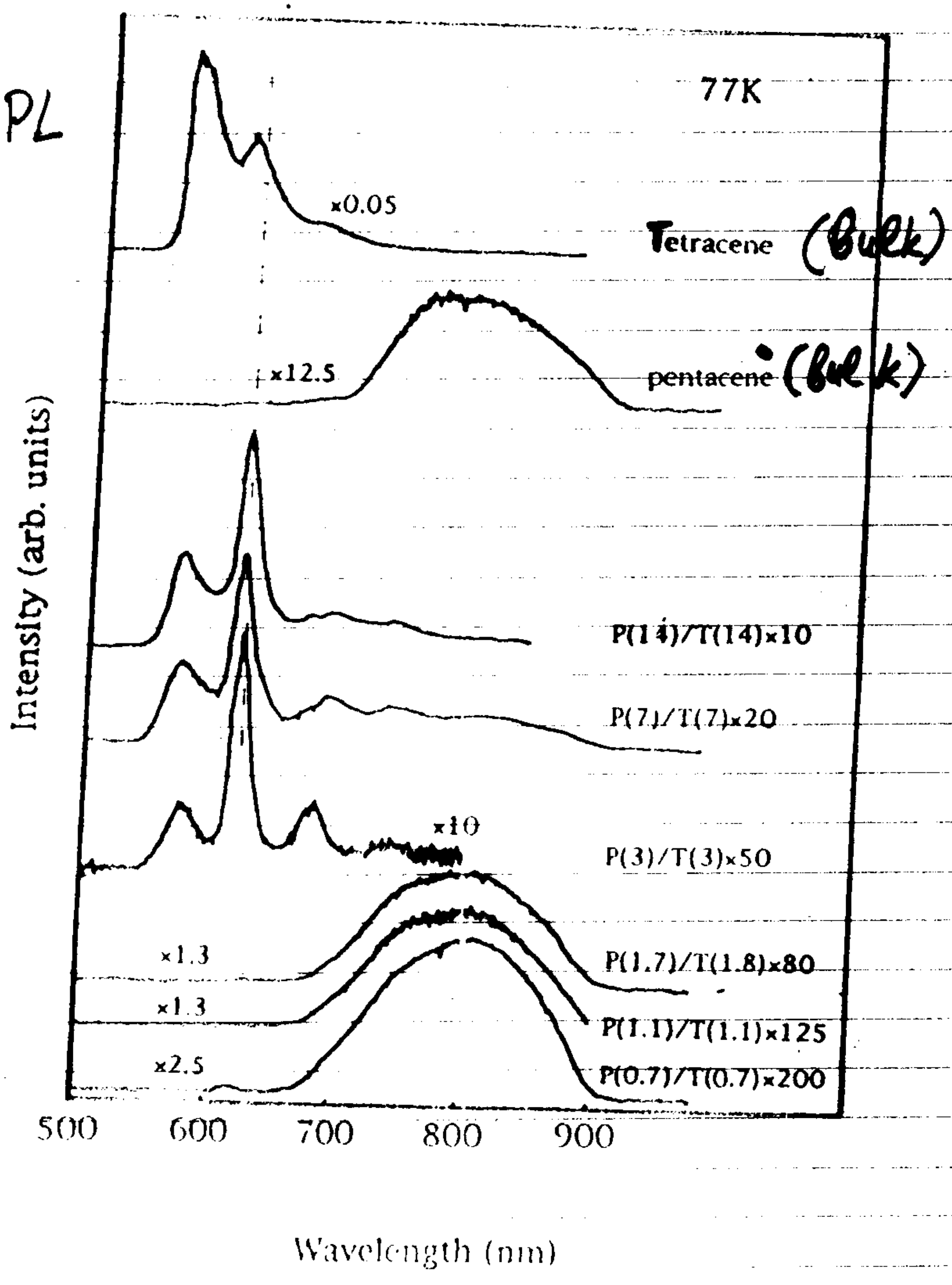
For n < 3 → Intermixing

H. Akimichi, T. Inoshita, S. Hotta, and H. Sakaki

Appl. Phys. Lett. 63 (20), 3158 (1993)

Pentacene/tetracene SL

Red shift!

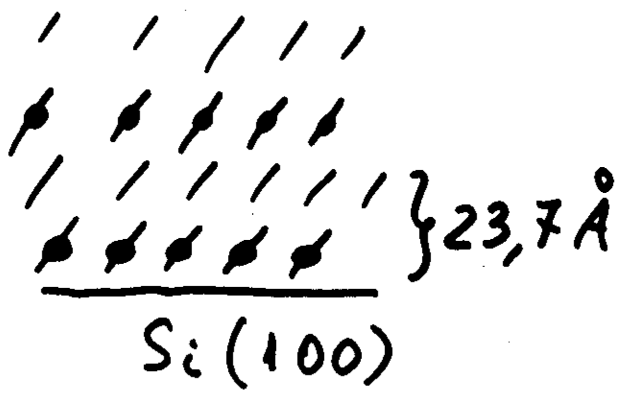


IG. 4. Photoluminescence spectra of pentacene/tetracene SL as well as rence pentacene and tetracene samples taken at 77 K.

(After H. Akimichi et al. Appl. Phys. Lett. 63(23), 3158 (1993)

T. Nonaka et al. Thin Solid Films
239 (1994) 214

Organic superlattice by alternate deposition of single molecular layers:



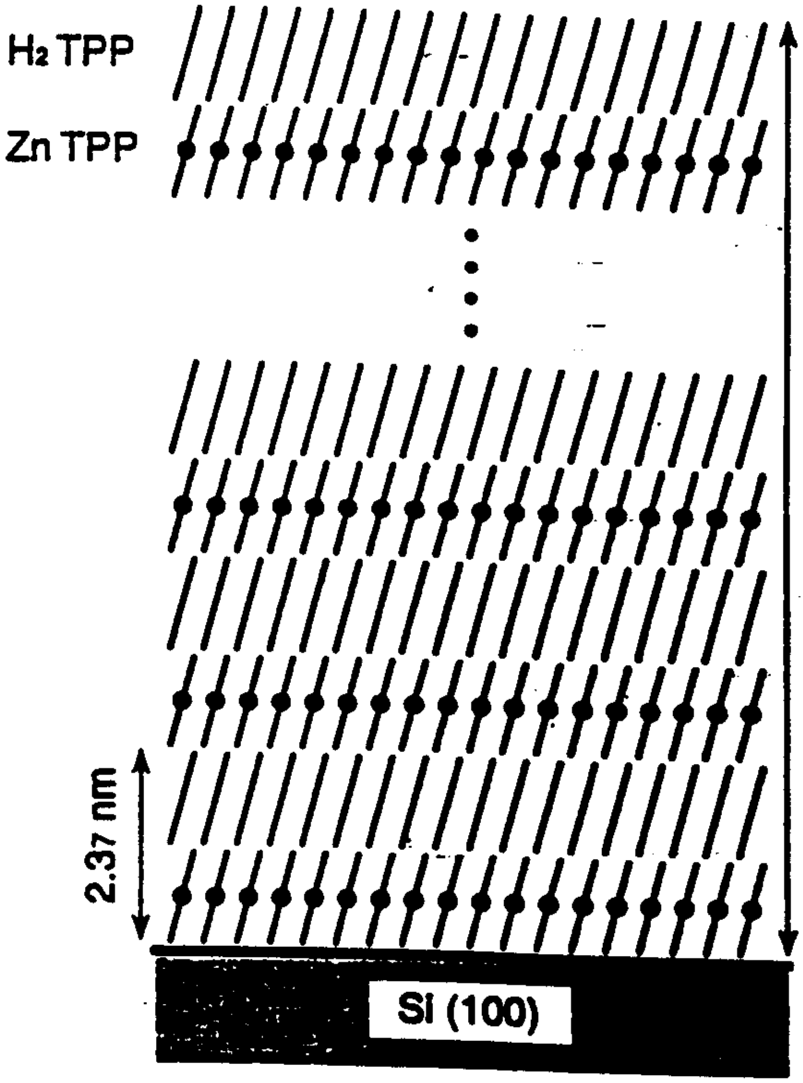
$C_{44}H_{30}N_4$
● tetraphenylporphyrin H_2TPP

/ $C_{44}H_{28}N_4Zn$

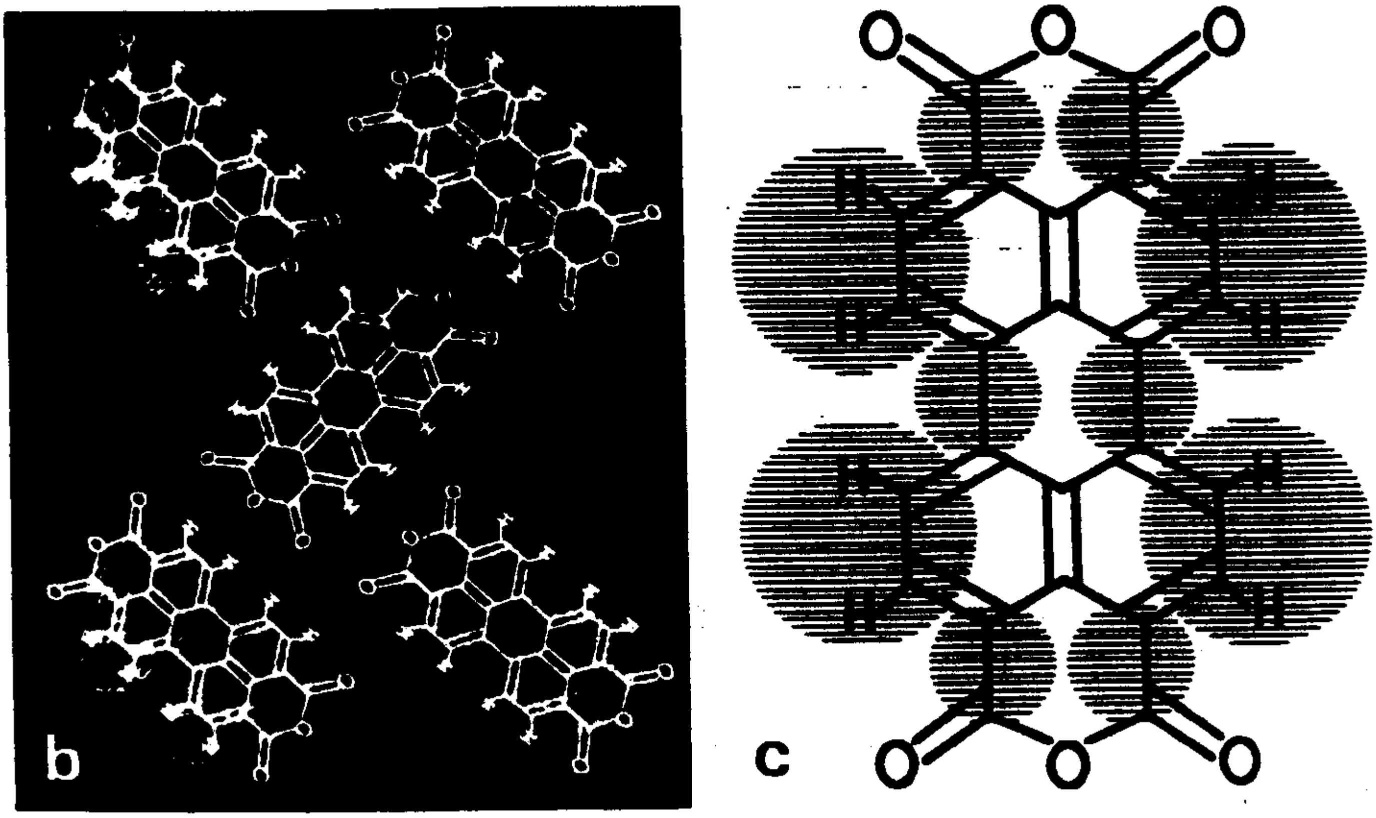
Y. Imanishi et al. Phys. Rev. Lett. 71, 2098 (1993)

Direct Observation of an Organic Superlattice Structure

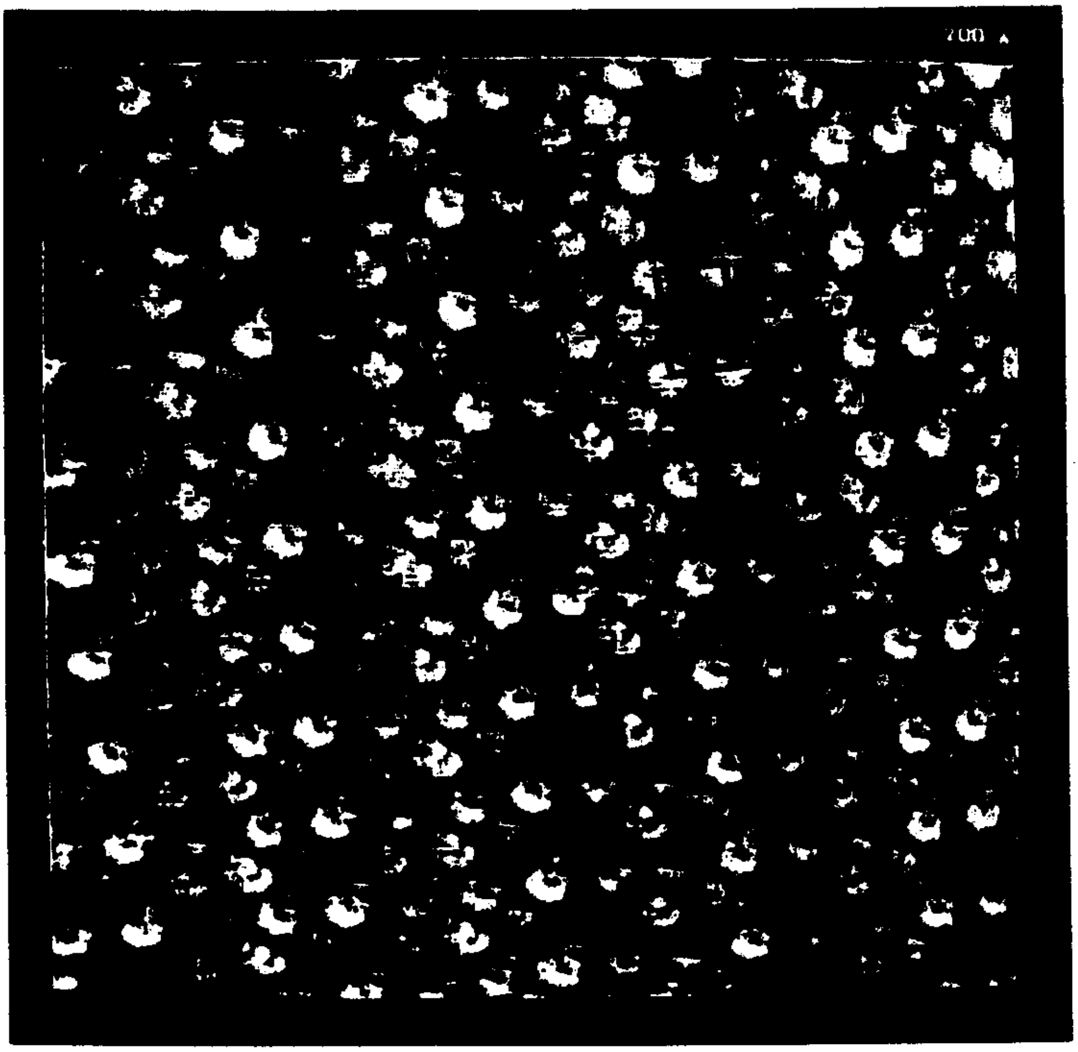
a. X-ray photoelectron spectroscopy
б. transmission electron microscopy



T. Tonaka, Y. Mori, N. Nagai, Y. Nakagawa, M. Saeda, T. Takahagi, and A. Ishitani, *Thin. Solid Films* **239** , 214 (1994)



C. Ludvig, B. Gompf, W. Glatz, J. Petersen, W. Eisenmeneger, M. Mobus, U. Zimmerman, and N. Karl, Zeitschrift fur Physik B 86, 397 (1992)



C. Ludvig, B. Gompf, W. Glatz, J. Petersen, W. Eisenmeneger, M. Mobus, U. Zimmerman, and N. Karl, <u>Zeitschrift fur Physik B</u> **86**, 397 (1992)

Frenkel - Wannier - Mott

The Bloch scheme describes independent motion of electrons and holes. In 1931 Frenkel went beyond the scope of this scheme in advancing the concept of excitons:

electron excitation waves which do not carry electric current.

Frenkel considered „small radius" excitons (electron and hole - on the same molecule or atom).

Wannier - another limiting case (1937):

the distance $r_{eh} >> a$, a - lattice cons

Effective mass approximation: $E_{kin} = \frac{\hbar^2 k^2}{2M}$

and e - h interaction $V(r) = -e^2/r$

Mott added in $V(r)$ (1938)

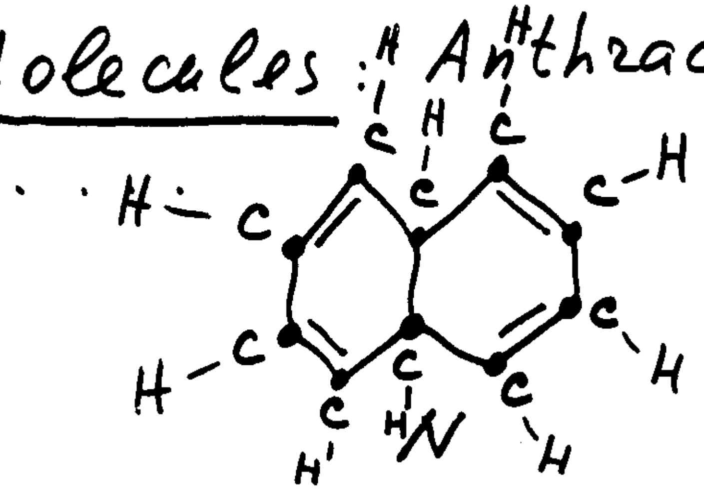
factor ϵ^{-1}, ϵ - macroscopic diel. constan

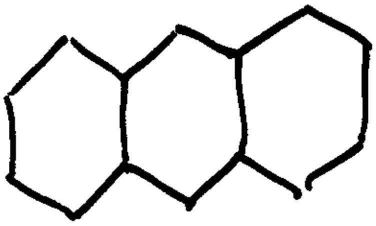
It was rigorously justified by

Sham and Rice (1966).

Excitations in molecular crystals.

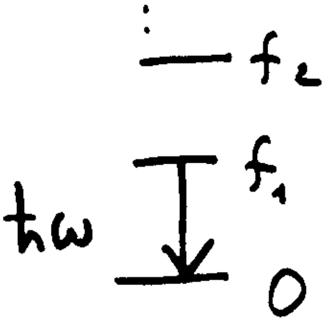
Molecules: Anthracen, Naphtalene,





A

a) Electronic excitations:



$\epsilon^{f_1}-\epsilon^{0} \simeq 2 \div 3 \div 4\,eV$

Singlet, triplet

For Anthracene $\varepsilon^{f_1}-\varepsilon^{f_0} \simeq 3,5\,eV$

b) Molecular Vibrations (Normale Modes):

$\Omega_1, \Omega_2, \dots \Omega_n. \quad \Omega \simeq 100 \div 3000\,cm$

$1\,eV \simeq 8000\,cm^{-1} \simeq 10\,000\,°K$

c) Ionization energy $I \simeq 5 \div 7\,eV$

$\omega_{Deb.} \simeq 50-70\,°K$

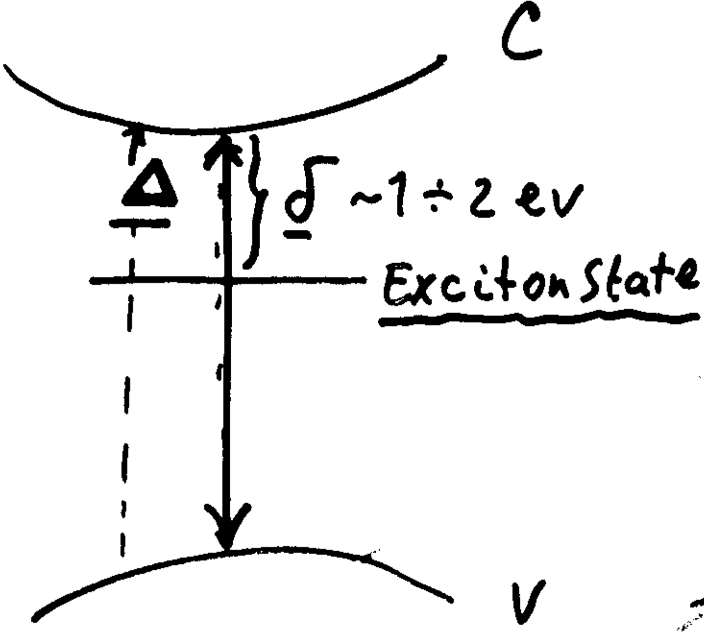
Molecular crystals:

Intermolecular interaction energy V

$V \approx 0.01 \div 0.05\ \mathrm{ev} \ll I$

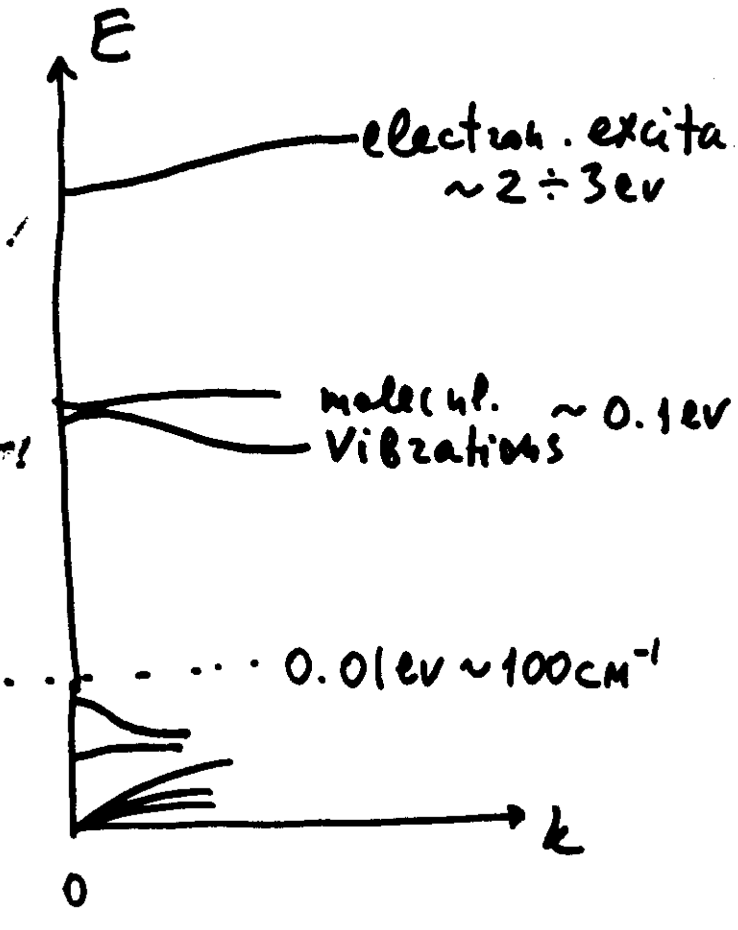
for ground state and for lowest energy excitations. V can be considered as weak perturbation.

Band gap picture:



$\Delta \sim 5\ \mathrm{ev}$, $\delta \sim 1 \div 2\ \mathrm{ev}$

Spectrum



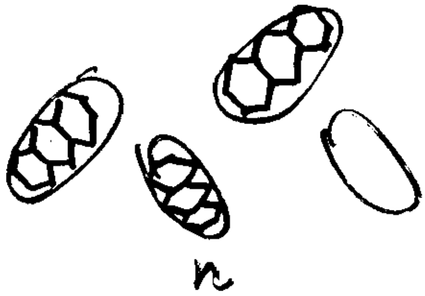
Electronic and vibrational excitons

Small radius excitations.

Excitons in Organics:

Frenkel and charge transfer (CT) Excitons:

Frenkel:



$$\chi_n^f = \varphi_n^f \prod_{m\neq n} \varphi_m^0$$

$$\hat{H}_{Mol.}\varphi^f = E^f\varphi^f, \quad f = 0, 1, \ldots$$

Ground State:

$$\Phi_0 = \varphi_1^0 \cdot \varphi_2^0 \cdots = \prod_n \varphi_n^0$$

$$\Psi_k = \frac{1}{\sqrt{N}} \sum_n \chi_n^f e^{i\vec{k}\vec{n}}$$

—— f ε^f

$E = E(k) =$ [illegible]

—— 0 , ε^0

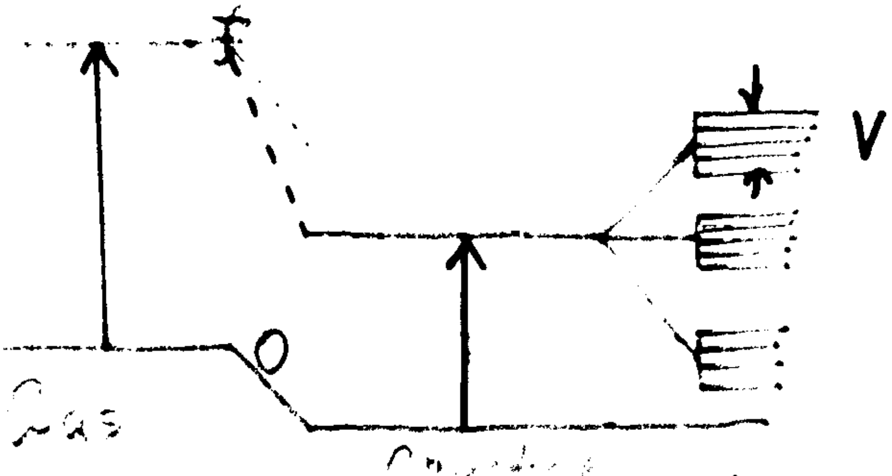
$$= \varepsilon^f - \varepsilon^0 + D + M(k)$$

Gas – Condensed Matter Shift, D<

$\varepsilon^f - \varepsilon^0 \sim 2 - 4$ eV, $D \approx 0.1$ eV

$$V \sim \frac{|p^{0f}|^2}{a^3} \sim 0.1\,\text{eV}$$

for strong 0→f transitions



Effective masses: for: $k \ll \frac{\pi}{a}$

$$\Delta(k) = \Delta(0) + \frac{\hbar^2 k^2}{2M}$$

f: $\Delta_{max} - \Delta_{min} \approx 500\,cm^{-1}$, $k_{max} \approx \frac{\pi}{a}$

$$2 \cdot \frac{\hbar^2}{2M}\left(\frac{\pi^2}{a^2}\right) \approx 500\,cm^{-1} \approx \frac{500 \cdot 1{,}6 \cdot 10^{-12}}{8000} = 1.6 \cdot 10^{-13}$$

$$M \approx \frac{2 \cdot \hbar^2 \cdot \pi^2 \quad m_0}{2\,a^2 \cdot 1{,}6 \cdot 10^{-13} \cdot m_0} \approx \frac{2 \cdot \cancel{10^{-27}} \cdot 10^{-27} \cdot 10}{3{,}2 \cdot 10^{-13} \cdot (8 \cdot 10^{-8})^2 \cdot \cancel{10^{-27}}} m_0 \approx$$

$$\approx \frac{2 \cdot 10^{-26}}{200 \cdot 10^{-13} \cdot 10^{-16}} m_0 \approx \underline{10\,m_0}. \quad \underline{M \approx 10\,m_0}$$

M is strongly dependent on direction of $\underline{\vec{k}}$.

M can be > 0 and < 0.

Exciton-phonon interaction:

Coherent and uncoherent excitons.

Mean free path ℓ: a) If $\underline{\ell \gg a}$, a - lattice constant

we have coherent ex-ns

$\delta k \sim \frac{1}{\ell} \ll k$

<u>k - good quantum number</u>

б) If $\underline{\ell \lesssim a}$

$\delta k \sim \frac{\pi}{a}$ - we have no coherent states

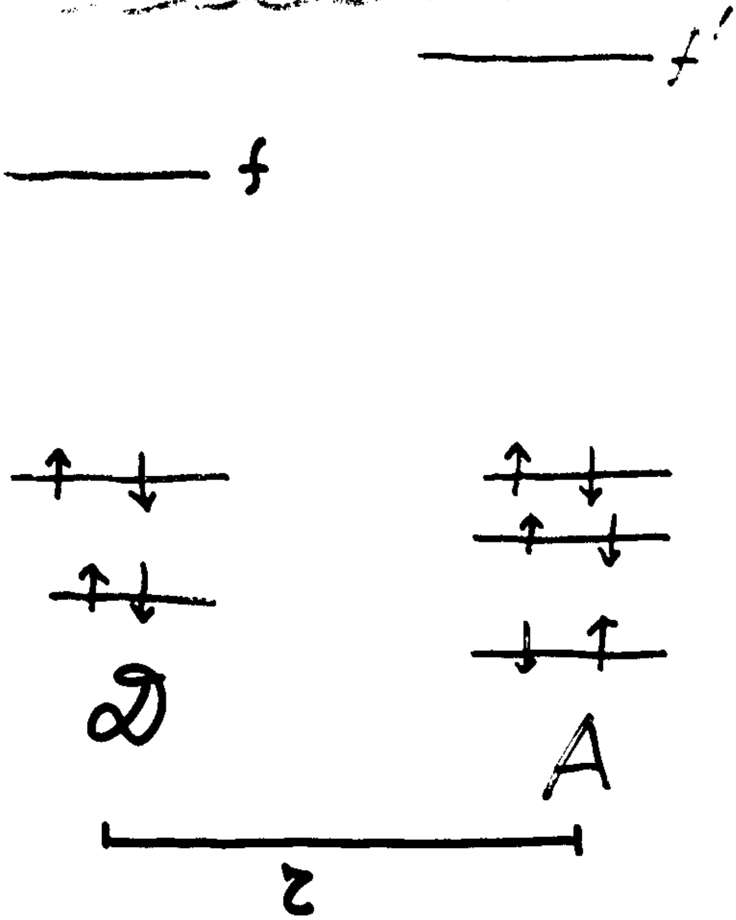
<u>is no more a good qu. numb.</u>

jumps from one site to another

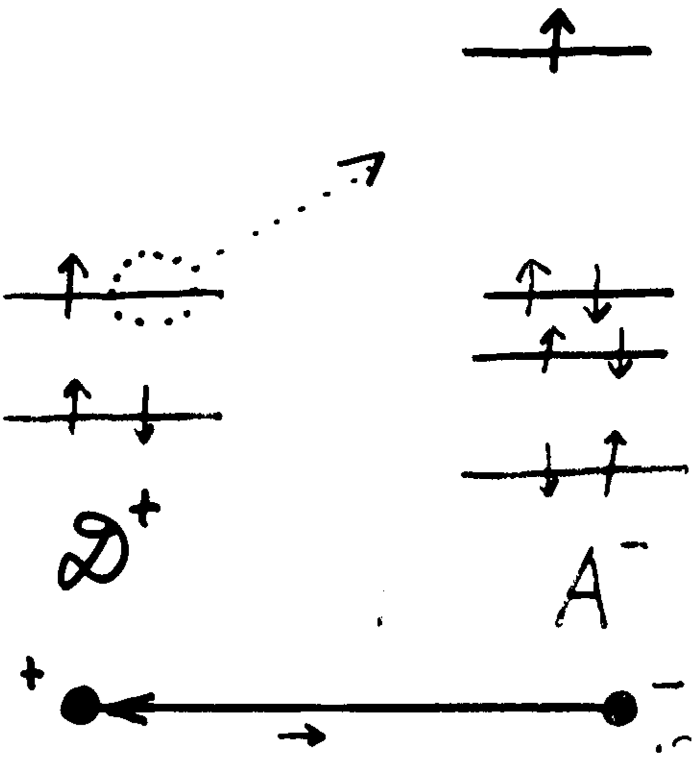
Charge Transfer Excitons
(CTE)
in Organics

Donors and Acceptors: CTE

a. Ground state:



b. Excited CT state:



→ the electron's level of A^-.

Dipole moment in exc. state:

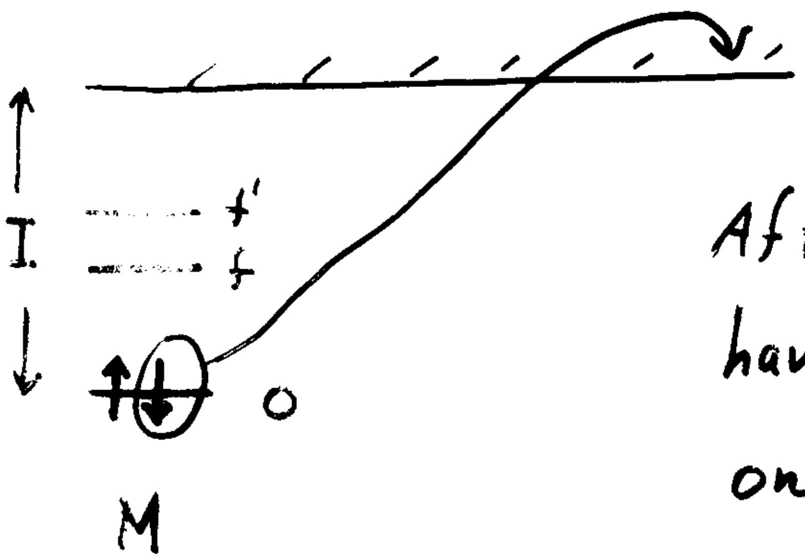
$\mu = er$

$e = 4.8 \; 10^{-10}$ CGSE

$r = 5A$

$\mu = 24 D, \; 1D = 10^{-1}$

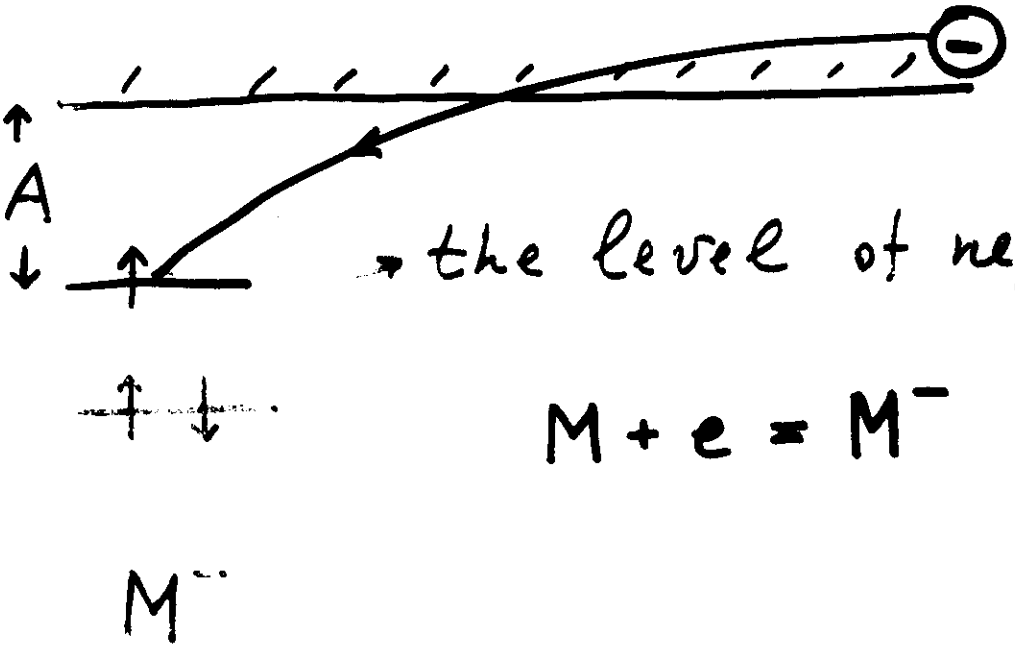
I - ionization energy



After ionization we have M^+ and electron on infinity.

$$M \rightarrow M^+ + e$$

A - electron affinity energy



$$M + e = M^-$$

Energy of CTE:

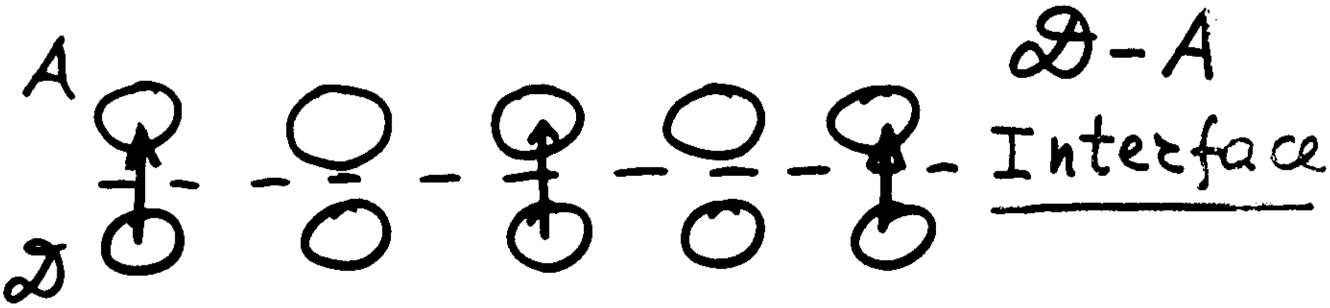
$$\Delta = I - A - \frac{e^2}{\epsilon r} + P$$

$I \sim 5eV$, $A \sim 3eV$, $\epsilon = 3$, $r = 5A$

$$\frac{e^2}{\epsilon r} = \frac{23\cdot 10^{-20}}{3\cdot\ 5\cdot 10^{-8}}\ \frac{1}{1.6\cdot 10^{-12}} \approx 1\,eV$$

In this case $\Delta \approx 5 - 3 - 1 \approx 1ev$

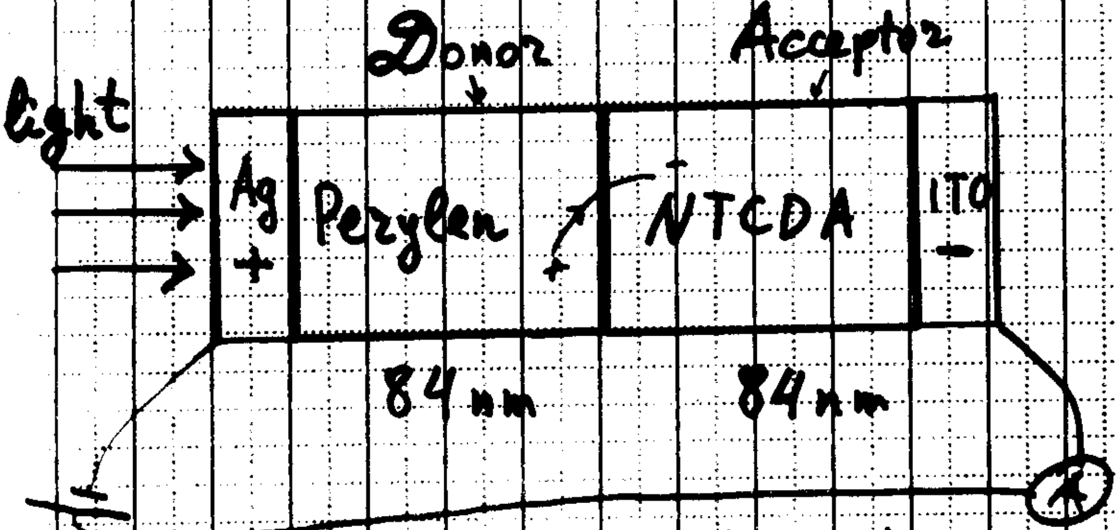
Assume ○ - donors, ⬭ - acceptors



All lowest energy CTEs have the same direction of dipoles: static dipoles in excited state.

Charge Separation at <u>Donor Acceptor Interfaces</u> in Thin Film Organic Photovoltaic Cells

<u>N. Karl</u> et al. (Uni Stuttgart)



„We conclude that <u>the charge carriers</u> that give rise to the external (short circuit) photocurrent <u>are predominantly generated at D−A interface</u>".

„exciton formation and <u>exciton migration to the D−A interface</u> is an <u>indispensable demand</u>".

Fermi Resonances:

$2\omega_1^A \approx \omega_2^B$, $\omega_1^A + \omega_2^A \approx \omega_3^B$, $3\omega_1 \approx \omega_2$;

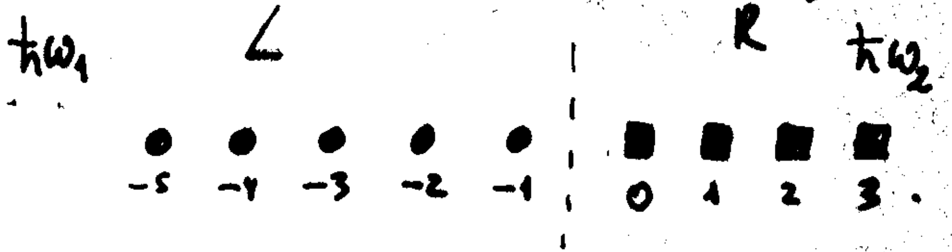
$2\omega_1 + \omega_2 \approx \omega_3$ and so on.

In the case of multilayer crystallin organic structures the spectrum of structure is created by the overlapping of the spectra of different crystalline compounds and new Fermi Resonances arise and can be useful due to the anharmonicity across the interfaces.

New interface modes:

FRIM: 1993 [illegible] 20, [illegible]

Fermi Resonance Interface Modes in Organic Multilayer Structures (+LB+copolymers).



1D model

$\omega_2 \approx 2\omega_1$

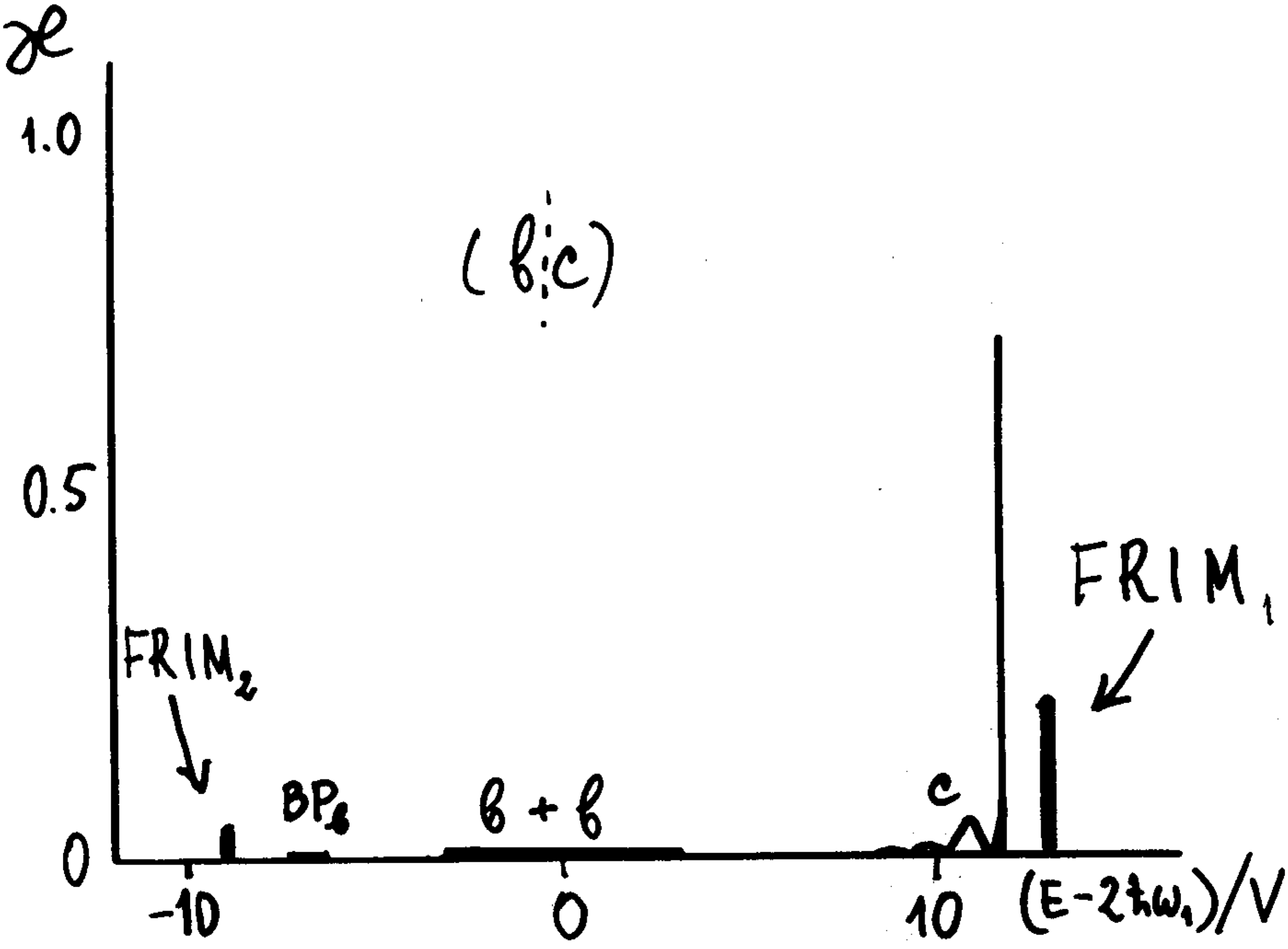
$$\hat{H}_L = \sum_{n<0} \hbar\omega_1 \overset{+}{b}_n b_n + \sum_{n<0,m<0} V_{nm} \overset{+}{b}_n b_m - A\sum_{n<0} (\overset{+}{b}_n)^2 b_n^2$$

$$\hat{H}_R = \sum_{n\geq 0} \hbar\omega_2 \overset{+}{C}_n C_n + \sum_{n\geq 0,m\geq 0} V_{nm} \overset{+}{C}_n C_m ,$$

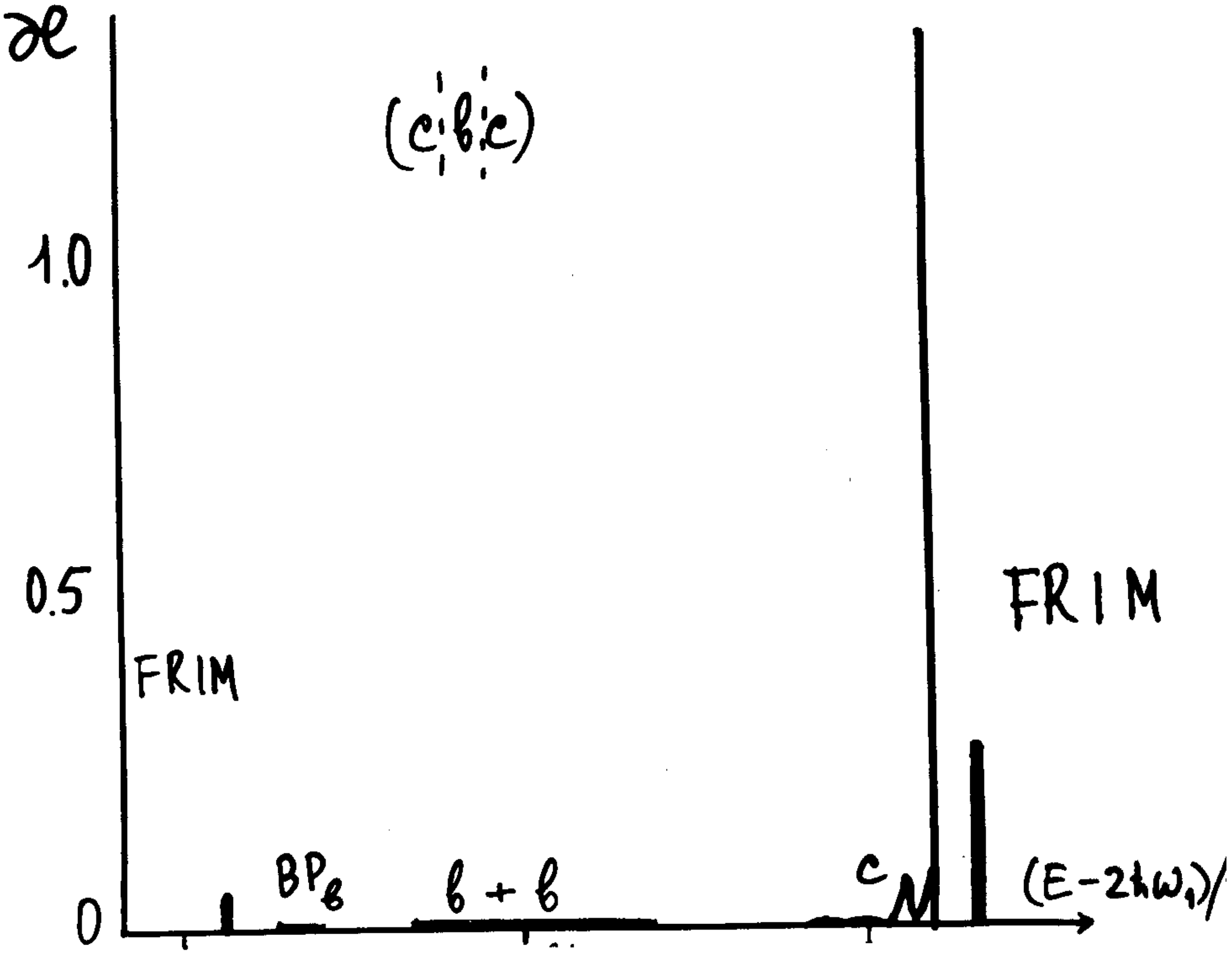
$$\hat{H}_{int} = \Gamma\left(\overset{+}{C}_0 b_{-1}^2 + \overset{+}{b}{}_{-1}^2 C_0\right)$$

$$\hat{H}_0 = \hat{H}_L + \hat{H}_R + \hat{H}_{int} , \quad \hat{H}_0 \Psi = E\Psi$$

$$\Psi = \sum_{n<0,m<0} \psi_{nm} \overset{+}{b}_n \overset{+}{b}_m |0\rangle + \sum_{n\geq 0} \varphi_n \overset{+}{C}_n |0\rangle .$$



ϰ
1.0
0.5
0
(b¦c)
FRIM$_1$
FRIM$_2$
BP$_b$
b + b
c
-10
0
10
(E-2ħω$_1$)/V



ϰ
(c¦b¦c)
1.0
0.5
0
FRIM
FRIM
BP$_b$
b + b
c
(E-2ħω$_1$)/

Fermi Resonance Interface Modes and Bistable Energy Transmisssion through the Interface

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Troitsk, 142092, Russia
★★ Department of Physics and Astronomy, Arizona State University. Tempe,
AZ 85287-1504, USA

Abstract

We investigate the nonlinear dynamics of an interface in the region of the interface Fermi resonance, when the energy $\hbar\omega_2$ of vibrational excitations on one side of the interface is approximately equal to $2\hbar\omega_1$, where $\hbar\omega_1$ is the excitation energy on the other side. We show that intermolecular cubic anharmonicity across the interface not only produces Fermi Resonance Interface Modes (FRIM), but can also lead to bistability in the energy transmission through the interface. Using the simplest $1D$ model for the interface, we demonstrate the close connection between the bistability and the classical version of the FRIM, together with the dependence of the bistability on the driving frequency and amplitude, and on the vibrational damping.

I.Introduction

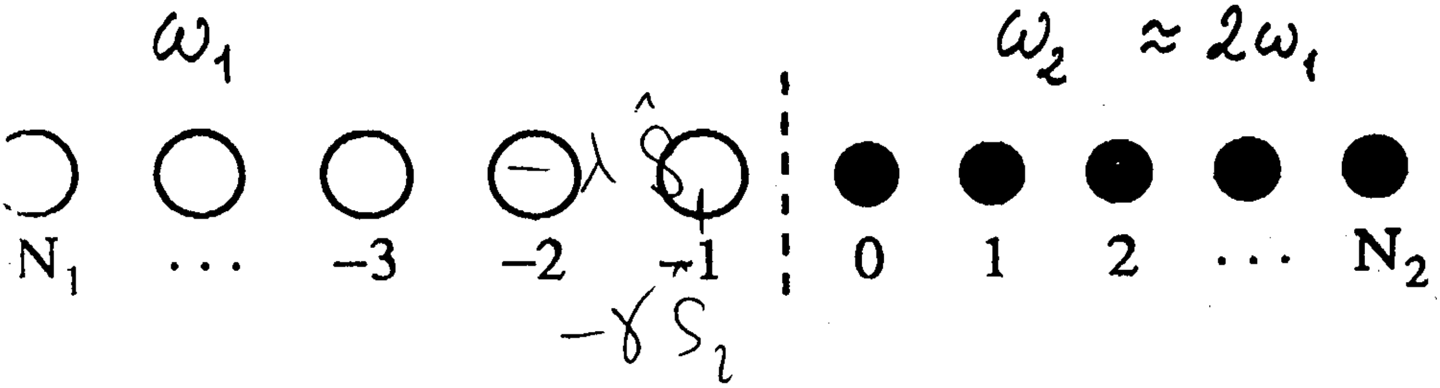
There is great current interest in the preparation of high quality organic thin films and multilayered structures for various electrical and optical model investigations aimed at potential future applications (see, e.g. [1-13] and references therein). However, the basic understanding of the linear and nonlinear optical properties of such structures remains to be achieved. One of us (V.A.) has recently stressed [14-15] that among the new features of such structures, not only the confinement of electrons and excitons, which are typical for inorganic multilayered structures, but also the nontrivial role of interfaces can be important. In some cases, such as donor-acceptor interfaces in Langmuir-Blodgett films [16-18], the electronic structure of the interfaces can be responsible for nonlinear optical properties. Of course in other cases the role of interfaces can be different. For example, it was shown [19] that in the multiple quantum well structures consisting of alternating layers of two crystalline organic semiconductors PTCDA and NTCDA, the observed blue-shift of the lowest singlet exciton line with decreasing layer thickness [1] can easily be understood (in terms of "small radius" excitons) if one takes into account the change of the gas/condensed- matter shift near the interface, together with the corresponding shift of the molecular electronic energy levels. Another example is the Fermi Resonance Interface Modes (FRIM), arising due to coupling across the interface between two different layered media [20]. The possibility

[illegible] 1993

183, 395 (1993)

BISTABILITY

OQW + Copolimers + LB films



the laser frequency

$S = (\ ) + (\ )$

$\omega_2 \approx \omega_1$, I_0 intensity of pumping.

Anharmonicity across the interface: SH

$\gamma \lambda \delta$

with bistability

Fig. 1

of energy through interface*) RPA:

$$\hat{H} = \hat{H}_0 - \sum_{n<0}\left(\overset{*}{\mu}\,\overset{+}{b}_n E e^{-i\omega_L t} + \mu b_n \overset{*}{E} e^{i\omega_L t}\right)$$

ω_L - the laser frequency, μ - the dipole transition element. Using: $i\hbar\dot{A}=[A,H]$ we have:

$$\hbar\dot{b}_n = -i\hbar\omega_1 b_n - i\sum_{m<0} V^{(1)}_{nm} b_m + i\overset{\delta_{n,-1}}{\swarrow}2\Gamma c_0 \overset{+}{b}_{-1} + i\overset{*}{\mu} E e^{-i\omega_L t}$$

$$\hbar\dot{c}_n = -i\omega_2\hbar c_n - i\sum_{m\geq 0} V^{(2)}_{nm} c_m - i\Gamma b_{-1}^2$$

Rotating frame

$$b_n = \tilde{b}_n e^{-i\omega_L t}, \quad c_n = \tilde{c}_n e^{-2i\omega_L t}:$$

$$\beta_n = \langle \tilde{b}_n \rangle, \quad \gamma_n = \langle \tilde{c}_n \rangle$$

$$\begin{cases} \hbar\dot{\beta}_n = -i\hbar(\omega_1-\omega_L)\beta_n - i\sum_{m<0} V^{(1)}_{nm}\beta_m + i2\Gamma\langle \tilde{c}_0 \overset{+}{b}_{-1}\rangle \delta_{-1,n} \\ \qquad + i\overset{*}{\mu}E \\ \hbar\dot{\gamma}_n = -i\hbar(\omega_2-2\omega_L)\gamma_n - i\sum_{m\geq 0} V^{(2)}_{nm}\gamma_m - i\Gamma\langle b_{-1}^2\rangle\delta_{0,n} \end{cases}$$

V. Agranovich and J. Page, PLA (1993) ~~submitted~~ 183, N5/6 395)

Intens. vibrations - left

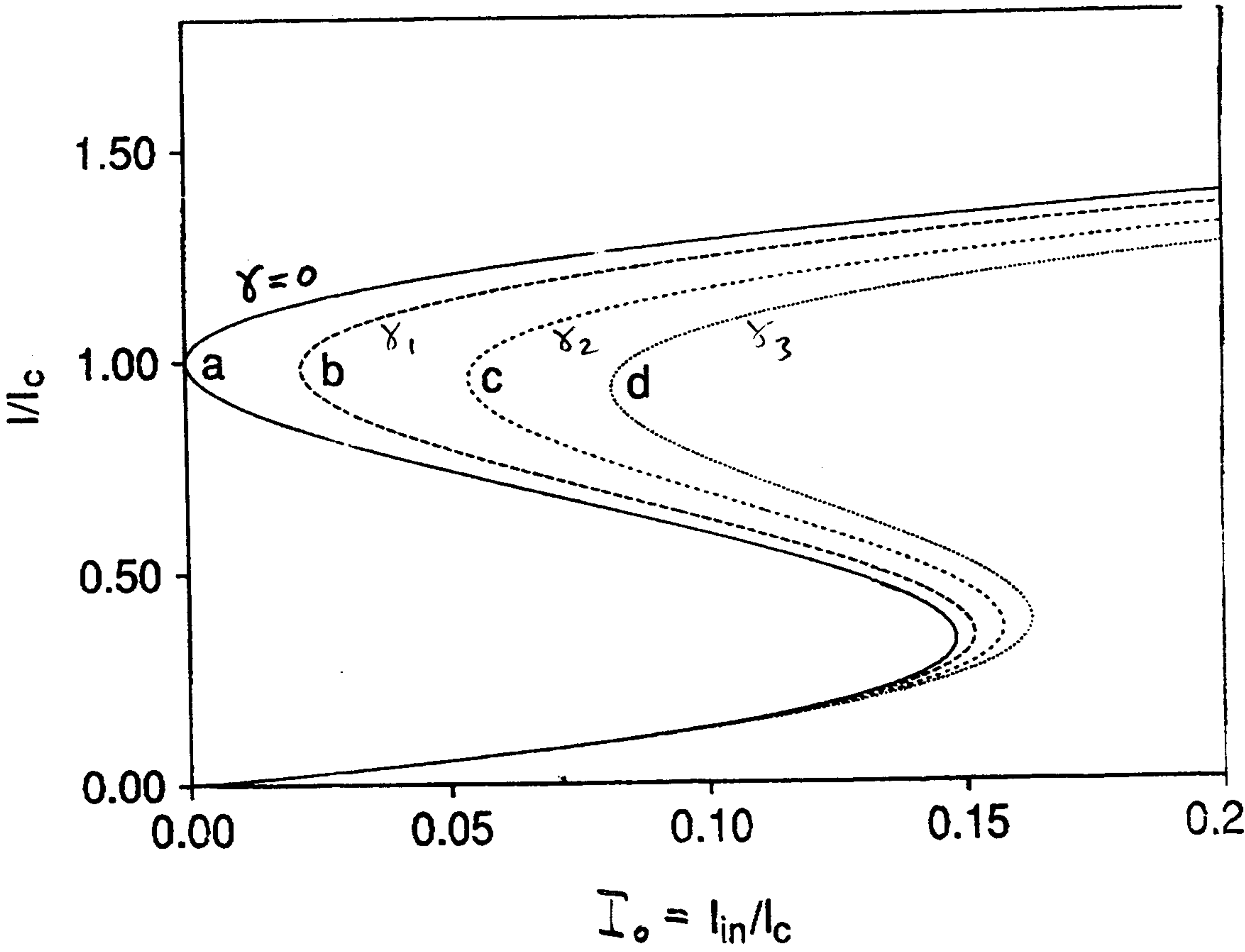


Fig. 2

Intensity vibrations- right

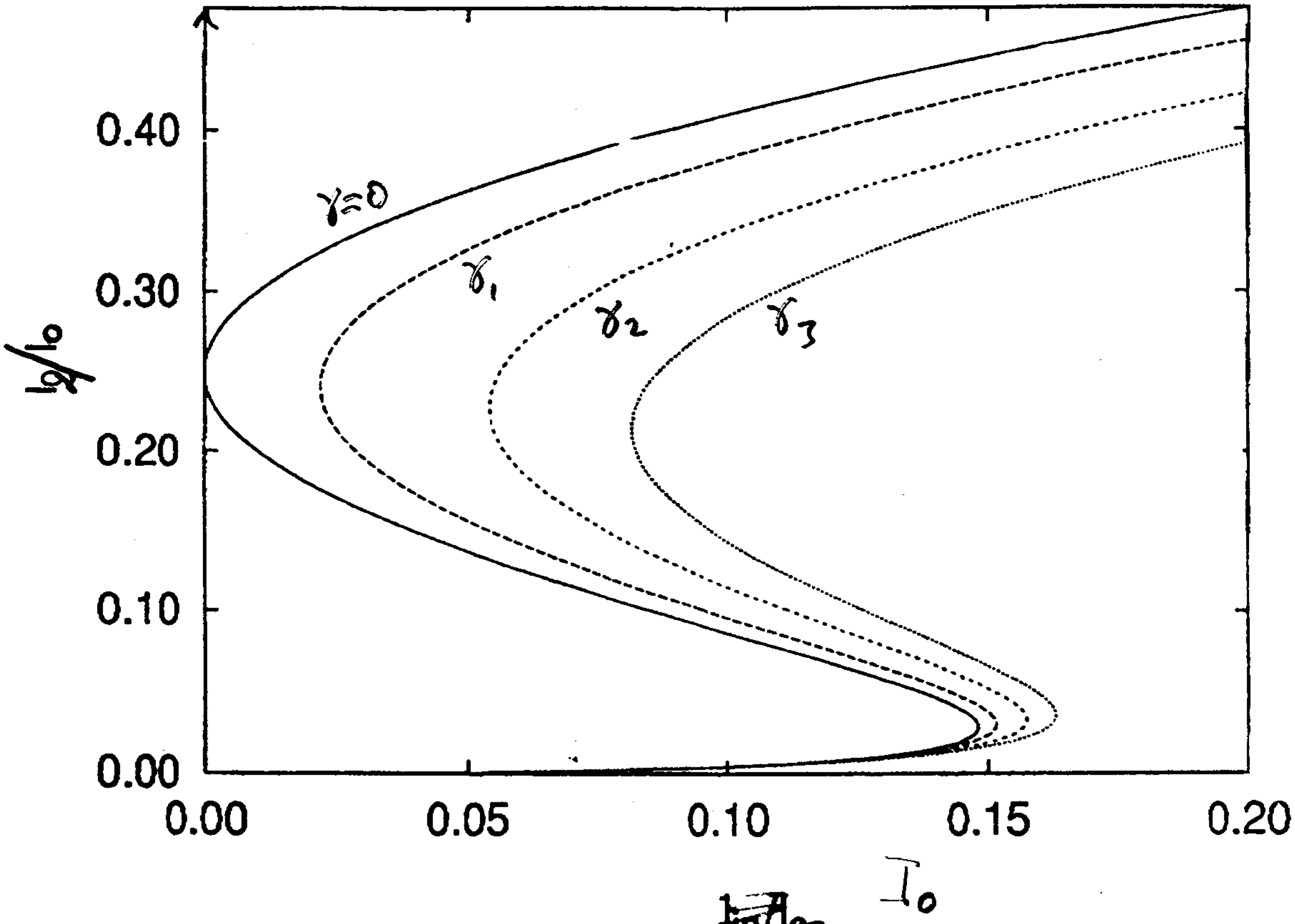
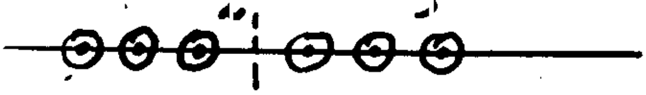


Fig. 3



MULTISTABILITY

$$\hat{H} = \hat{H}_A + \hat{H}_B + \hat{H}_c + \hat{H}_{ABc} + \hat{H}_{int}(t)$$

$$\hat{H}_A = \sum_{n<0} \hbar\omega_1 \overset{+}{a}_n a_n + \sum_{n,m<0}{}' V_{nm}^{(a)} \overset{+}{a}_n a_m$$

$$\hat{H}_B = \sum_{n<0} \hbar\omega_2 \overset{+}{b}_n b_n + \sum_{n,m<0}{}' V_{nm}^{(b)} \overset{+}{b}_n b_m$$

$$\hat{H}_c = \sum_{n\geq 0} \hbar\omega_3 \overset{+}{c}_n c_n + \sum_{n,m\geq 0}{}' V_{nm}^{(c)} \overset{+}{c}_n c_m$$

$$\hat{H}_{ABc} = \Gamma\left(a_{-1} b_{-1} \overset{+}{c}_0 + c_0 \overset{+}{a}_{-1} \overset{+}{b}_{-1} \right)$$

$$\hat{H}_{int} = -\sum_{n<0} \hat{P}_n E(n,t),$$

$$\hat{P}_n = \mu_1 a_n + \mu_2 b_n + h.c.$$

$$E(n,t) = E^{(1)} \exp\{i(k_1 n - \omega_L^{(1)} t)\} +$$

$$+ E^{(2)} \exp\{i(k_2 n - \omega_L^{(2)} t)\} + h.c.$$

two laser beams: $\omega_L^{(1)} \approx \omega_1$, $\omega_L^{(2)} \approx \omega_2$

Random Phase Approximation:

$$\hat{H}_{int} = -\sum_{n<0} \Big\{ (\overset{*}{\mu}_1 E^{(1)}) \overset{+}{a}_n \exp\{-i\omega_L^{(1)} t\} +$$

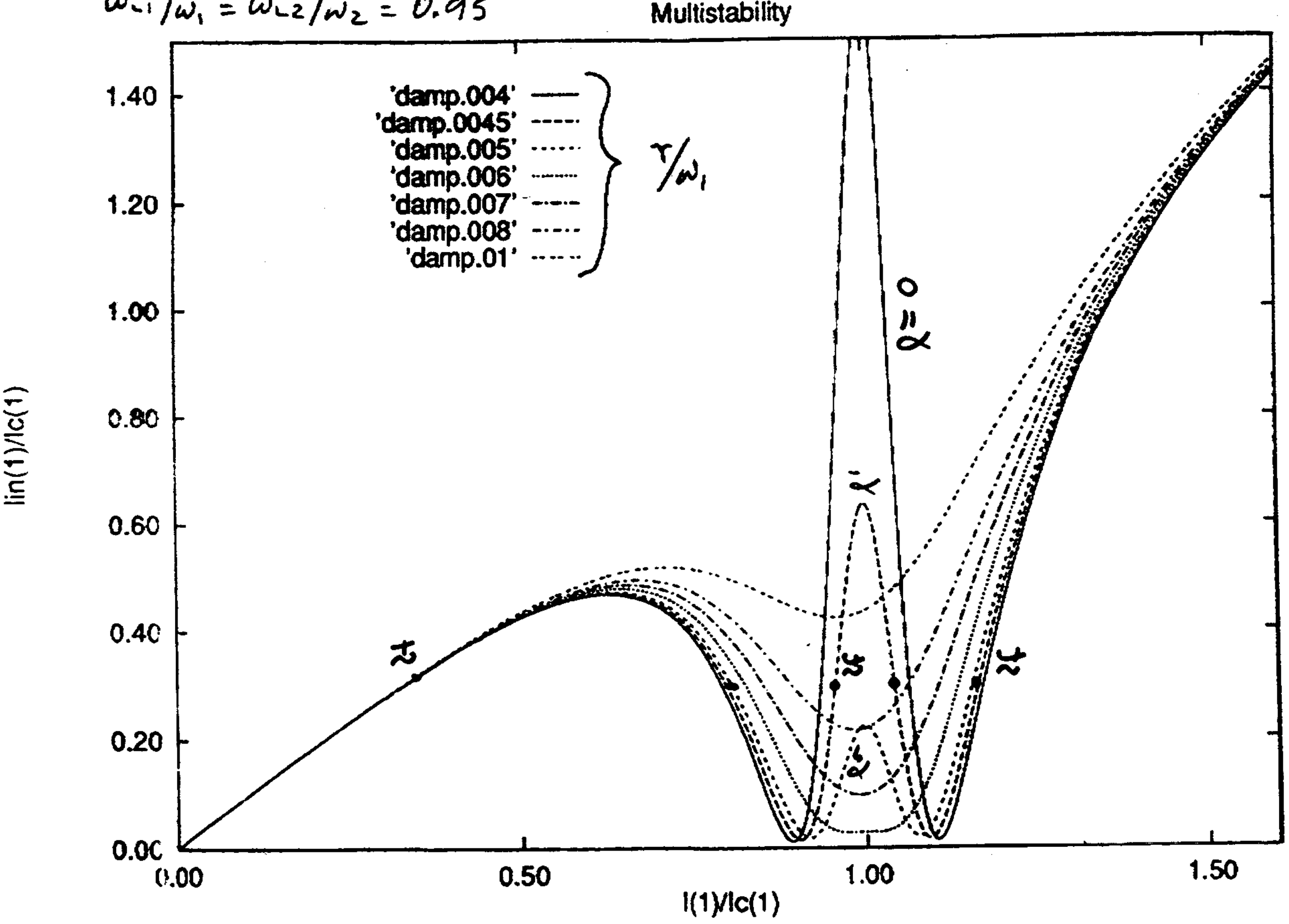
$$+ (\overset{*}{\mu}_2 E^{(2)}) \overset{+}{b}_n \exp\{-i\omega_L^{(2)} t\} + h.c. \Big\}.$$

We assume, that c-vibration is dipole forbiden: $\mu_3 = 0$.

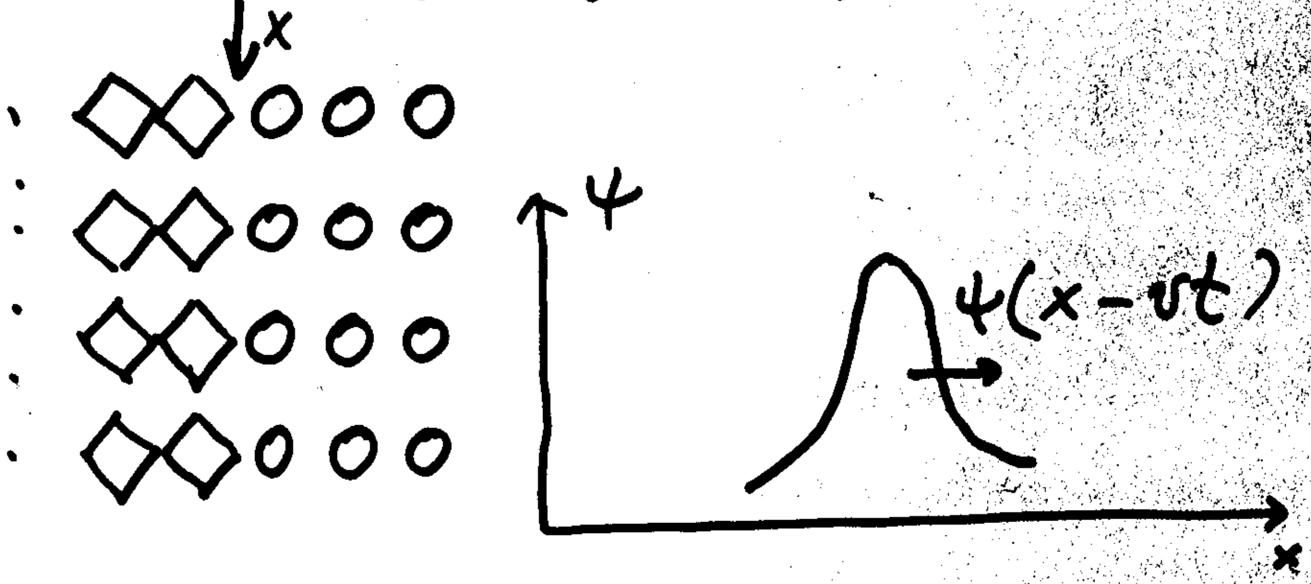
Two lasers: $\omega_L^{(1)} \approx \omega$ $\omega^{(2)} \approx \omega$

$\omega_1/\omega_2 = 0.75$ $I_{in}(2)/I_c(2) = 0.02$, $\omega_1+\omega_2=\omega_3$

$\omega_{L1}/\omega_1 = \omega_{L2}/\omega_2 = 0.95$



We also found recently the Fermi Resonance Interface Solitons*) propagating along the interface:



*) V. Agranovich, A. Kamchatnov Sov. Phys. JETP Letters (1994) ~~submitted~~

$$a_n = \tilde{a}_n \exp\{-i\omega_L^{(1)} t\},\quad b_n = b_n \exp\{-i\omega_L^{(2)} t\}$$

$$c_n = \tilde{c}_n \exp\{-i(\omega_L^{(1)} + \omega_L^{(2)}) t\}$$

$$\hbar \dot{\tilde{a}}_n = i\Big\{ (\hbar\omega_L^{(1)} - \hbar\omega_1)\tilde{a}_n - \sum_{n,m<0} V_{nm}^{(1)} \tilde{a}_m + (\overset{*}{\mu}_1 E^{(1)}) - \\ - \Gamma C_0 \overset{+}{b}_{-1}\, \delta_{-1,n} \Big\}$$

$$\hbar \dot{\tilde{b}}_n = i\Big\{ (\hbar\omega_L^{(2)} - \hbar\omega_2)\tilde{b}_n - \sum V_{nm}^{(2)} \tilde{b}_m + (\overset{*}{\mu}_2 E^{(2)}) - \\ - \Gamma C_0 \overset{+}{a}_{-1}\, \delta_{-1,n} \Big\}$$

$$\hbar \dot{\tilde{c}}_n = i\Big\{ (\hbar\omega_L^{(1)} + \hbar\omega_L^{(2)} - \hbar\omega_3)\tilde{c}_n - \sum V_{nm}^{(3)} \tilde{c}_m - \\ - \Gamma a_{-1} b_{-1} \delta_{n,0} \Big\}$$

$$\alpha_n = \langle a_n \rangle,\quad \beta_n = \langle b_n \rangle,\quad \gamma_n = \langle c_n \rangle$$

$$\alpha_{-1} = G_{-1,-1}^{(1)}(\Delta_1)\,\Gamma\gamma_0 \overset{*}{\beta}_{-1} - (\overset{*}{\mu}_1 E^{(1)}) \sum_{m<0} G_{-1\,m}^{(1)}(\Delta_1)$$

$$\beta_{-1} = G_{-1,-1}^{(2)}(\Delta_2)\,\Gamma\gamma_0 \overset{*}{\alpha}_{-1} - (\overset{*}{\mu}_2 E^{(2)}) \sum_{m<0} G_{-1,m}^{(2)}(\Delta_2)$$

$$\gamma_0 = G_{0,0}^{(3)}(\Delta_3)\,\Gamma \alpha_{-1} \beta_{-1}$$

or

$$\left.\begin{aligned} \alpha_{-1} &= \Gamma^2 G_{-1,-1}^{(1)}(\Delta_1) G_{0,0}^{(3)}(\Delta_3) |\beta_{-1}|^2 \alpha_{-1} - \Omega_1 \\ \beta_{-1} &= \Gamma^2 G_{-1,-1}^{(2)}(\Delta_2) G_{0,0}^{(3)}(\Delta_3) |\alpha_{-1}|^2 \beta_{-1} - \Omega_2 \end{aligned}\right\}$$

$$\Omega_1 = (\overset{*}{\mu}_1 E^{(1)}) \sum_{m<0} G_{-1,m}^{(1)}(\Delta_1),\quad \Omega_2 = (\overset{*}{\mu}_2 E^{(2)}) \sum_{m<0} G_{-1,-1}^{(2)}(\Delta_2)$$

$$\left.\begin{aligned} I_1(1-\mathcal{D}_1 I_2)^2 &= |\Omega_1|^2 \\ I_2(1-\mathcal{D}_2 I_1)^2 &= |\Omega_2|^2 \end{aligned}\right\}$$

$$\left.\begin{aligned} \mathcal{D}_1 &= \Gamma^2 G^{(1)}_{-1,-1}(\Delta_1)\, G^{(3)}_{0,0}(\Delta_3) \\ \mathcal{D}_2 &= \Gamma^2 G^{(2)}_{-1,-1}(\Delta_2)\, G^{(3)}_{0,0}(\Delta_3) \end{aligned}\right\}$$

$\Delta_1 = \hbar(\omega_L^{(1)} - \omega_1),$

$\Delta_2 = \hbar(\omega_L^{(2)} - \omega_2),$

$\Delta_3 = \hbar(\omega_L^{(1)} + \omega_L^{(2)} - \omega_3).$

$$I_2 = |\Omega_2|^2 / (1 - \mathcal{D}_2 I_1)^2$$

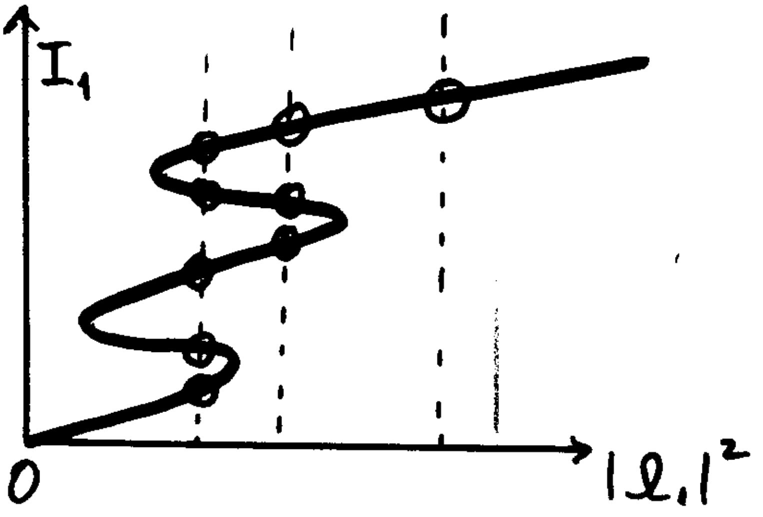
$$I_1\left\{1 - \mathcal{D}_1 \frac{|\Omega_2|^2}{(1-\mathcal{D}_2 I_1)^2}\right\}^2 = |\Omega_1|^2$$

or

$$\underline{I_1\left[(1-\mathcal{D}_2 I_1)^2 - \mathcal{D}_1|\Omega_2|^2\right]^2 = |\Omega_1|^2(1-\mathcal{D}_2 I_1)^4 -}$$

Fifth order eq-n for I_1.

$$I_3 = |\gamma_0|^2 = \Gamma^2 \left|G^{(3)}_{0,0}(\Delta_3)\right|^2 \frac{I_1|\Omega_2|^2}{(1-\mathcal{D}_2 I_1)^2} \sim I_1 I_2 .$$



<u>Multistability</u> in nanostructure for <u>sum frequency</u> <u>generation</u>:

$\omega = \omega^{(1)} + \omega^{(2)}$

The Fermi resonances open up unique possibilities to create optically multistable system.

Conclusions

Hybrid interface excitons in organic-inorganic quantum wells

V. Agranovich, R. Atanasov, F. Bassani

We investigate the exciton states at the interface of organic and inorganic quantum wells (QW) , when the energy of the 2D Frenkel exciton in the organic QW is approximately equal to the energy of the 2D Wannier exciton in the inorganic semiconductor QW. We demonstrate that the dipole-dipole resonance interaction is responsible for the appearence of new states: mixed Frenkel-Wannier excitons with very unusual properties. These states can have large oscillator strengths, which are typical of Frenkel excitons, and at the same time they can have large exciton radiuses, typical for Wannier-Mott excitons. The dispersion curves display a minimum away from the center of the Brilluin zone, which is expected to influence the optical properties. The necessary characteristics of organic and inorganic crystals are discussed in order to obtain appropriate materials for studying hybrid states. Some illustrative calculations are performed for an organic layer deposited on a ZnCdSe quantum wells.

Interaction between an OOW and IOW

The total Hamiltonian H of this system may be written in the form

$$\hat{H} = \hat{H}_F + \hat{H}_W + \hat{H}_{int} ,$$

where the Frenkel-exciton Hamiltonian is

$$\hat{H}_F = \sum_{k,l} E_l^F(k) A_l^+(k) A_l(k) ,$$

and analogously the Wannier-Mott exciton Hamiltonian is

$$\hat{H}_W = \sum_{k,l} E_l^W(k) B_l^+(k) B_l(k)$$

The operator H_{int} may be written in the form

$$\hat{H}_{int} = \sum_{ll'} \langle F l k | \hat{V} | W l' k \rangle A_l(k) B_{l'}^+(k) + h.c.$$

where $\hat{V}$ is an interaction energy operator.

Let's consider the case when for some fixed l and l'

the difference $| E_l^F - E_{l'}^W |$

is small in comparison with the distance to the other exciton bands.

In this case, we look for the solutions of the Schr"odinger equation which are combinations of the nearest exciton bands only, and we can write

$$\Psi_k = A_\ell \Psi_\ell^F(k) \Phi_{1QW} + B_{\ell'} \Psi_{\ell'}^W(k) \Phi_{0QW},$$

where Φ_{0QW} (Ψ^F) and Φ_{1QW} (Ψ^W) are the corresponding ground (excited) state wave functions of noninteracting QWs .

In the case of thin organic and inorganic QW's, we may consider the mixing between the lowest exciton states only. Thus, we omit indexes ℓ , ℓ' and write the Schr"odinger equation as a system of two equations for the amplitudes A and B; $A[E^F - E] + B\langle F | H_{int} | W \rangle = 0$,

$$A\langle W | \hat{H}_{int} | F \rangle + B[E^W - E] = 0.$$

The condition for non zero solutions of the above system is given by the expression

$$[E^F(k) - E][E^W(k) - E] - |\langle F, k | \hat{H}_{int} | W, k \rangle|^2 = 0,$$

which determines the energies of the new hybrid Frenkel-Wannier (FW) exciton states.

When the system is in a hybrid state, it could be both in FE state and in WE state with the corresponding weight coefficients.

They can be evaluated from the condition that Ψ_K is normalized, i.e.

$$|A|^2 + |B|^2 = 1,$$

Thus, we obtain

$$|A|^2 = \frac{\Gamma^2(k)}{(E^F - E)^2 + \Gamma^2(k)}, \quad |B|^2 = \frac{(E^F - E)^2}{(E^F - E)^2 + \Gamma^2(k)}$$

where the parameter

$$\Gamma(k) = |\langle F, k | \hat{H}_{int} | W, k \rangle.$$

describes the FE-WE interaction strength. The only parameter we need to calculate the hybrid FW exciton states is the interaction parameter

$$\Gamma(k).$$

From it we can also obtain the average exciton radius as the expectation value of $\hat{R}$:

$$R(k) = a^F |A(k)|^2 + \lambda |B(k)|^2,$$

where a^F is the 2D-Frenkel exciton radius, and λ is the radius of the 2D-Wannier exciton under consideration. Usually, $\lambda >> a^F$ and for strongly hybrid states

$$R(k) \approx \lambda |B(k)|^2 > a^F.$$

Interaction parameter $\Gamma(k)$

$$\hat{H}_{int} = -\sum_n \hat{\vec{P}}_n \hat{\vec{E}}(n),$$

$$\hat{\vec{P}}_n = \vec{P}^{0f}(A_n^+ + A_n)$$

$$\Psi^F(k) = \frac{1}{\sqrt{N}} \sum_n \chi_n^f e^{-i\vec{k}\vec{n}}$$

$$\chi_n^f = \varphi_n^f \prod_{m \neq n} \varphi_m^0$$

$\text{——}\ f \quad \varphi_n^f$

$\text{——}\ 0 \quad \varphi_n^0$

$$\langle F,k;0|\hat{H}_{int}|0;W,k\rangle =$$

$$= -\sum_n \underline{\langle F,k|\hat{P}_n|0\rangle}\,\underline{\langle 0|\hat{\vec{E}}(n)|W,k\rangle}$$

$$\langle F,k|\hat{P}_n|0\rangle = \frac{\vec{P}^{0f}}{\sqrt{N}} e^{+i\vec{k}\vec{n}}$$

$$\langle 0|\vec{P}(\bar{z})|w,k\rangle = -\frac{1}{\lambda\sqrt{S}}\vec{D}(k)\,A(z)\,e^{-i\vec{k}\bar{z}}$$

$$D_p(k) = \frac{C_{p\beta}\, e\hbar}{E^{w}(k)}\left(\frac{E_K}{\pi m_0}\right)^{1/2}$$

E_K - the Kane's energy

$p = x, y, z$, $\beta = hh, lh$ valence bands

$C_{xhh} = 1/\sqrt{2}$, $C_{xlh} = 1/\sqrt{6}$, $C_{zhh} = 0$,

$C_{zlh} = \sqrt{2/3}$

Assume, $k \parallel x$. In this case:

$\underline{\rho(\bar{z}) \neq 0}$ only for $\vec{D} \parallel z$ (Z-modes)

or for $\vec{D} \parallel x$ (L-modes)

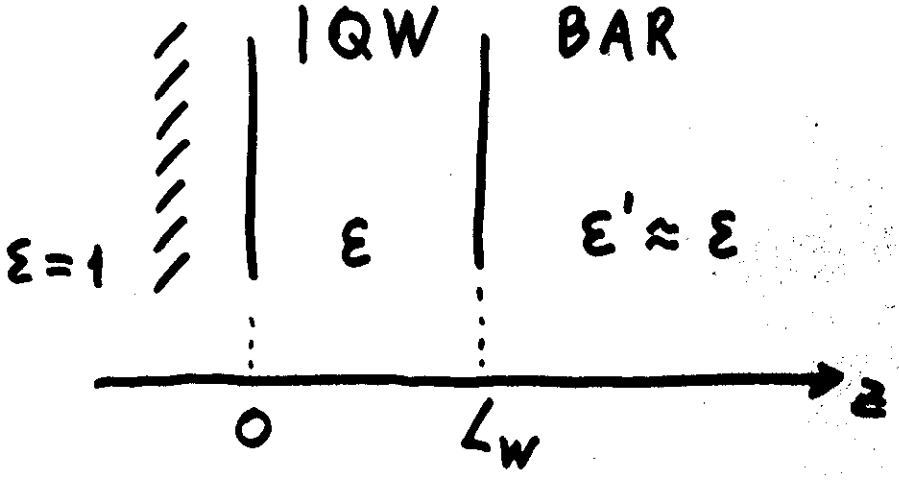
For $\vec{D} \parallel Y$ (T-modes) $\underline{\rho = 0}$

$$\hat{E}(\vec{r}) \longrightarrow \hat{P}(\vec{r})$$

$$\vec{E}(\vec{r}) \quad \rightarrow \langle 0|\hat{\vec{E}}(\vec{r})|Wk\rangle \rightarrow \langle 0|\hat{\vec{P}}(r)|Wk\rangle$$

$$\underline{\vec{E}(\vec{r}) = -\mathrm{grad}\,\varphi} \, , \quad \underline{\varepsilon\Delta\varphi = 4\pi\rho(\vec{r})}$$

$$\rho(\vec{r}) = \mathrm{div}\langle 0|\hat{\vec{P}}(\vec{r})|W,k\rangle$$



$\rho(\vec{r}) \neq 0$ only for $0 \leq z \leq L_w$

(the approximation of an <u>infinitely deep IQW</u>):

$$\langle 0|\hat{\vec{P}}(r)|W,k\rangle = -\frac{1}{\lambda\sqrt{S}}\vec{D}(k)A(z)e^{-i\vec{k}\vec{r}}$$

$$A(z) = 2\sin^2(\pi z/L_w)\Big/L_w$$

A. $\vec{D} \parallel z$ (Z-modes)

$$P_z(z,x) = -\frac{D_z A(z)}{\lambda\sqrt{S}}\, e^{-ikx} \quad , \quad \varphi(z,x) = f(z)\, e^{-ikx}$$

$$\varepsilon(z)\left(f'' - k^2 f\right) = -4\pi \frac{D_z}{\lambda\sqrt{S}} \frac{dA}{dz} \, ;$$

For $z < 0$:

$$f(z) = \frac{2\pi D_z\, q^2}{\lambda\sqrt{S}\, L_w k (q^2+k^2)} K(\varepsilon, k)\, e^{kz} \, , \quad q = \frac{2\pi}{L_w}$$

$$K(\varepsilon, k) = \frac{1 - e^{-kL_w}}{(\varepsilon+1)/2}$$

$$E_z = iE_x \, ; \quad E_z = -\frac{2\pi D_z\, q^2 K(\varepsilon,k)}{\lambda L_w \sqrt{S}\,(q^2+k^2)}\, e^{kz-ikx}$$

$$\Gamma_Z(k) = \frac{2\pi D_z \sqrt{(P_x^{0f})^2 + (P_z^{0f})^2}}{a\lambda L_w} \, \frac{q^2 K(\varepsilon,k)}{q^2+k^2}\, e^{-kz_0} \, ,$$

a - lattice constant
in OQW

$$\Gamma_L(k) = \frac{2\pi D_x \sqrt{(P_x^{0f})^2 + (P_z^{0f})^2}}{a\lambda L_w} \, \frac{q^2 K(\varepsilon,k)}{q^2+k^2}\, e^{-kz_0} \, .$$

Hybrid Exciton Dispersion Curves

$$E^{W}(k) = E^{W}(0) + \hbar^2 k^2/2M \ , \quad M = m_e + m_h$$

$$E^{F}(k) \simeq E^{F}(0)$$

$$E_{u,l}(k) = E^{W}(0) + \frac{\Delta}{2} + \frac{\hbar^2 k^2}{4M} \pm$$

$$\pm \sqrt{\left(\frac{\Delta}{2} - \frac{\hbar^2 k^2}{4M}\right)^2 + \Gamma^2(k)}$$

$$\Delta = E^{F}(0) - E^{W}(0)$$

For $k = k_0$, $\dfrac{\Delta}{2} = \dfrac{\hbar^2 k_0^2}{4M}$

$$E_{u,l} = E_0 \pm \Gamma_0 \ , \quad E_0 = E^{W}(k_0) = E^{F}(0)$$

$$|A_{u,l}| = |B_{u,l}| = \frac{1}{\sqrt{2}}$$

$ZnSe/Zn_{0.69}Cd_{0.31}Se$: L-modes

$L_w = 1\,nm$ $M = 0.32\,m_0$, $\lambda_{hh} = 4\,nm$

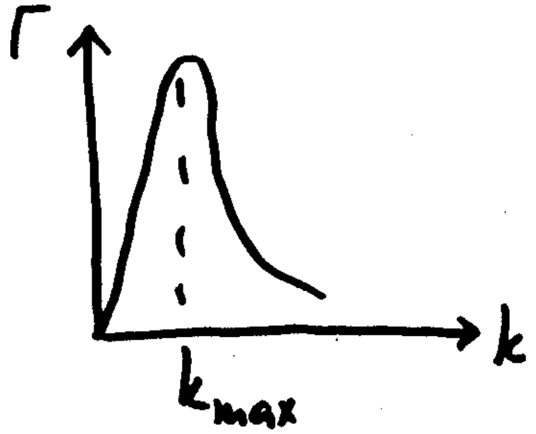
$E^{w}_{11lh} = 2{,}7\,eV$

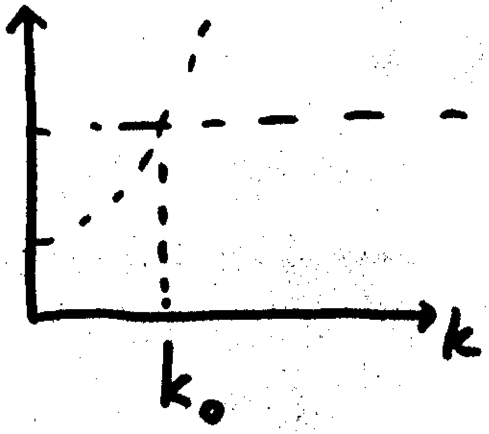
OQW: $P^{ot} = 5\,D$, $z_0 = 0.5\,nm$.

Discussions

1) $\Gamma(k) \sim e^{-kz_0}\left(1-e^{-kL_w}\right)$

$\frac{d\Gamma}{dk} = 0$ at $\underline{k_{max} = \frac{1}{L_w}\ln\left(1+\frac{L_w}{z_0}\right)}$





$k_{max} \approx k_0$ - in this case we may expect a maximum effect

2) Minimum in $E(k)$ away from $k=0$.

3) $2\Gamma(k_{max}) >> \delta_{0QW}, \delta_{1QW}$.

<u>In our case $2\Gamma \simeq 12$ meV, $\delta_{1QW} \simeq 1$ meV.</u>

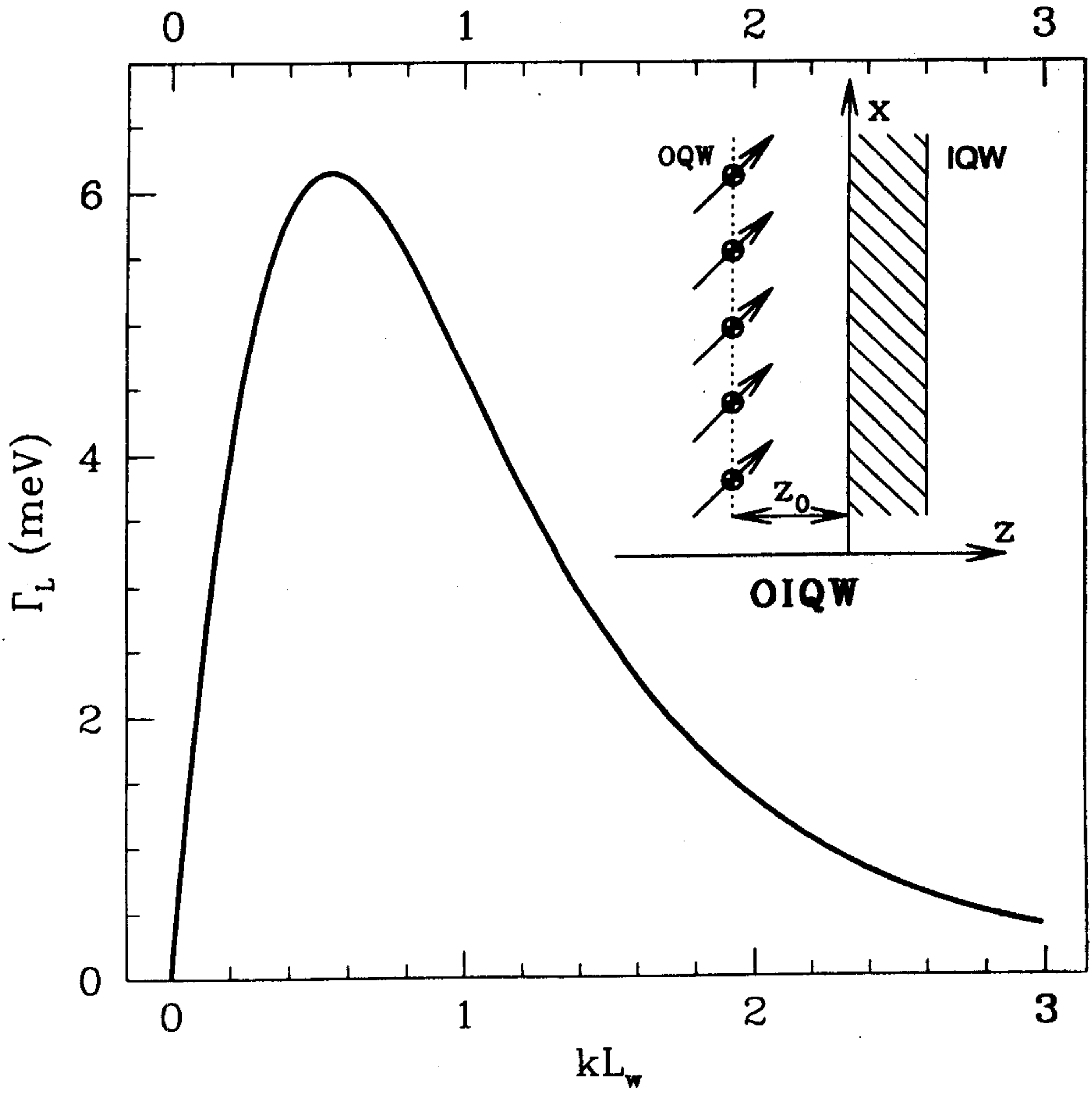
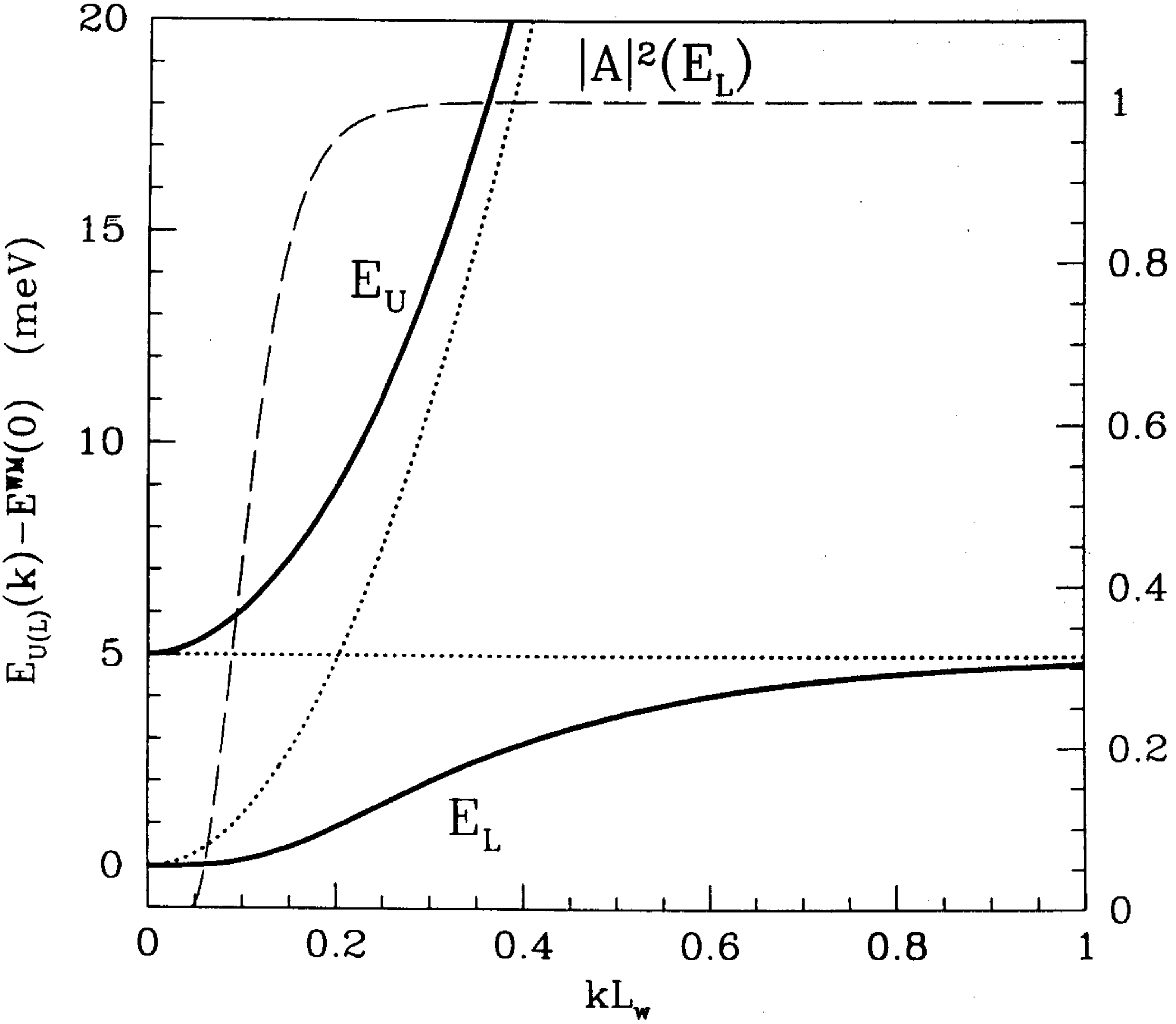


Fig. 1



20
15
10
5
0
$E_{U(L)}(k)-E^{WM}(0)$ (meV)
0
0.2
0.4
0.6
0.8
1
kL_w
1
0.8
0.6
0.4
0.2
0
$|A|^2(E_L)$
E_U
E_L

Fig. 2

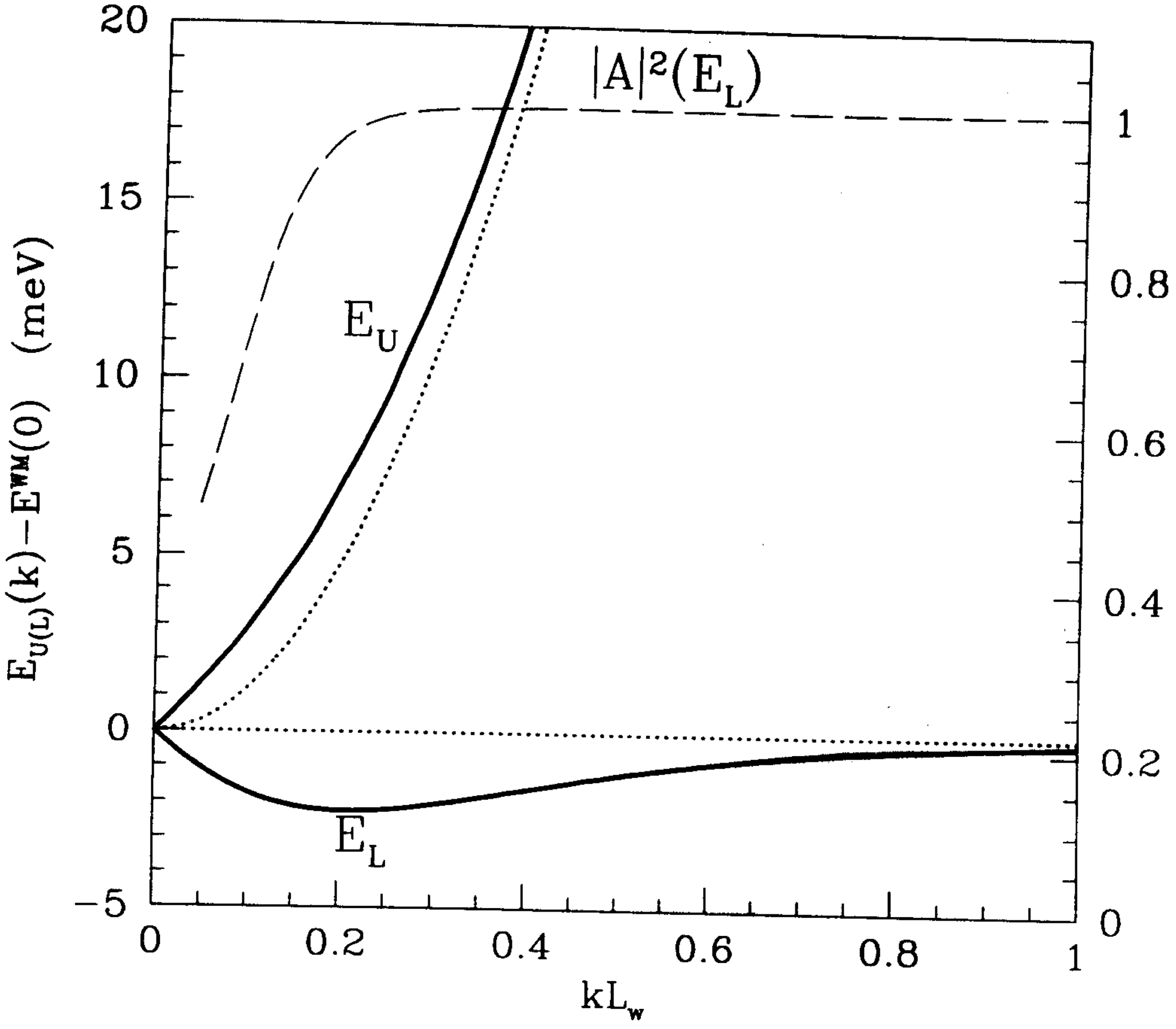

20
15
10
5
0
−5
$E_{U(L)}(k) - E^{WM}(0)$ (meV)
$|A|^2(E_L)$
1
0.8
0.6
0.4
0.2
0
E_U
E_L
0
0.2
0.4
0.6
0.8
1
kL_w

Fig 3

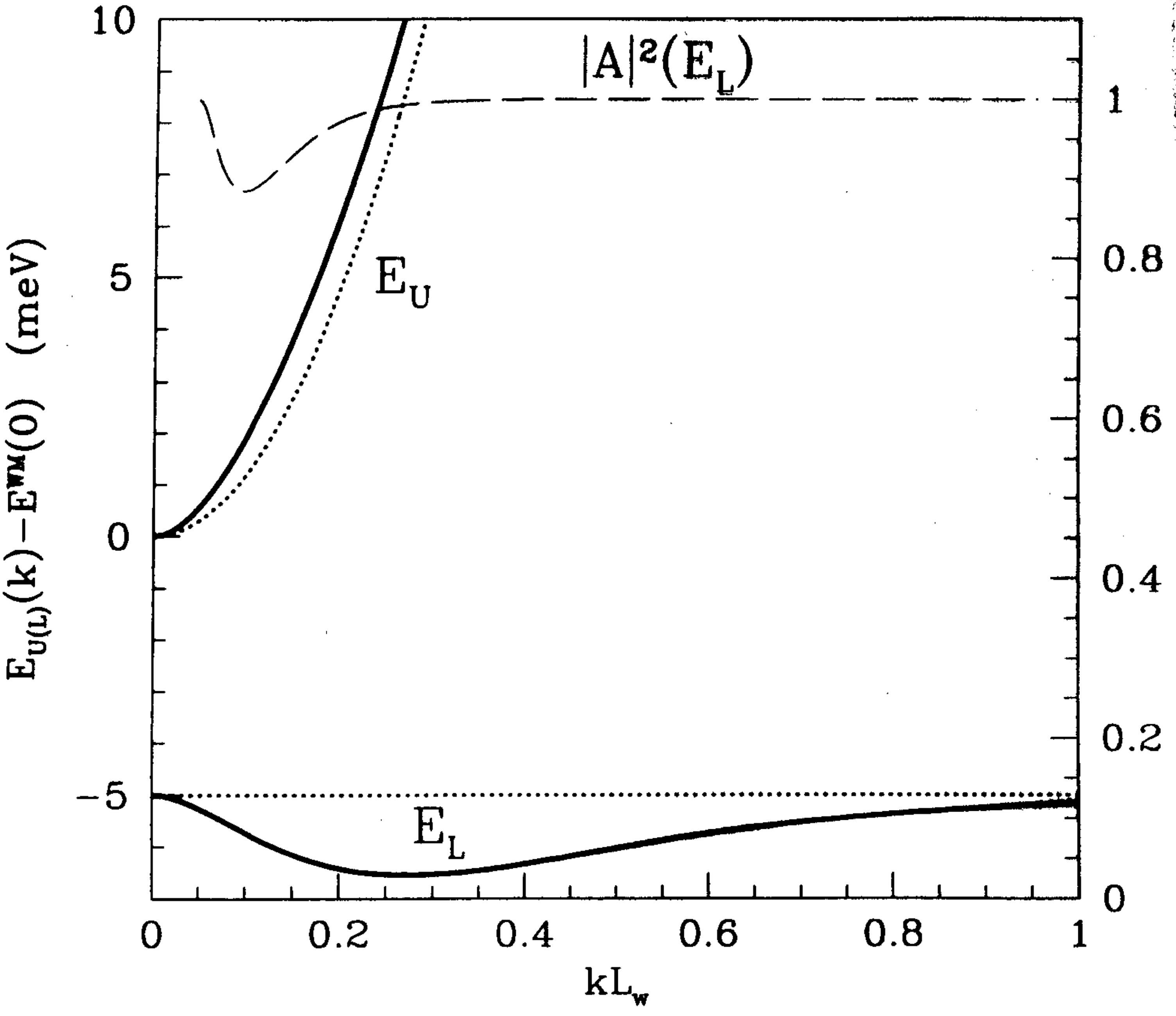


Fig 4

Dielectric-Metal Phase Transition in the System of Interacting Charge-Transfer Excitons.

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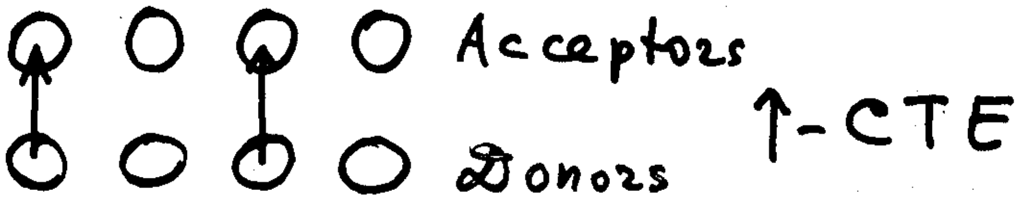
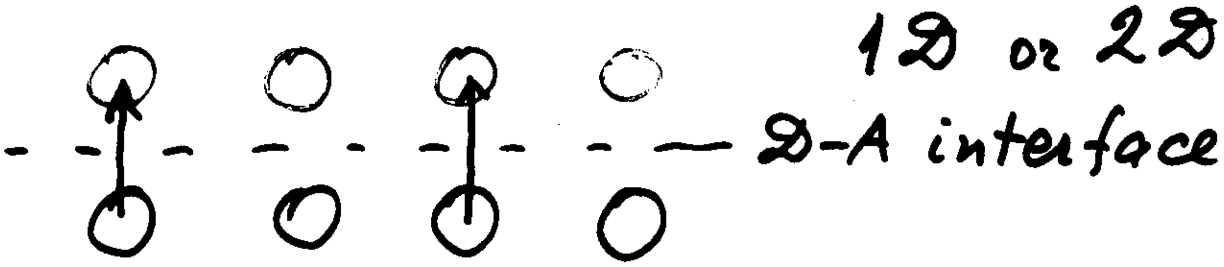
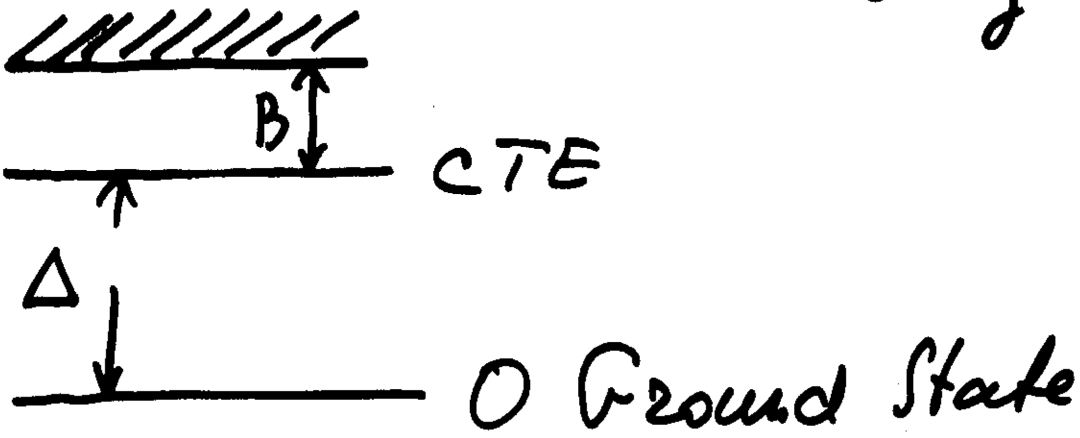


We demonsrate that strong dipole- dipole repulsion of <u>1D and 2D</u> charge transfer excitons (CTE) can induce at sufficintly high exciton concentrations an electron dielectric-metal phase transition.

$V_{int} \sim \mu^2/d^3$ can be order 1 eV.



$V_{int} = \mu^2/d^3 > 0$ - repulsion only



$\Delta \sim 2eV, \quad B < 0.5eV$

$V_{int} \approx 1eV$ for nearest CTE.

Repulsion induced electronic phase transition to conducting state at high concentration of CTE.

Simple model for temperature T=0.

To clarify the main idea we consider the simplest case of temperature T=0 and recall that above the excited state of a CTE the excited states of a crystal (interface) are always present which correspond to an electron and a hole spaced at an infinite distance.

In fact, the CTE energy is known to be:

$$\Delta = I - A - \frac{e^2}{\epsilon r} + P,$$

where I is the ionization energy of the donor, A is the acceptor electron affinity, r is the distance between an electron and a hole, ϵ is the static dielectric constant, P is the lattice polarization energy which is not included in the Coulomb interaction term. Assuming here a comparatively large electron-hole separation we neglect the term in the CTE energy arising from overlap of the electronic wave functions of donor and acceptor.

Temperature T=0 and long-range dipole-dipole interaction

To illustrate the above said we calculate with the simplest assumptions the total energy of the system $E(n_1, n_2)$ for the case of two- dimensional interface. Here n_1 is the number of CTEs, and n_2 is the number of dissociated electron-hole pairs:

$$n_1 + n_2 = n,$$

where n is the total number of excitations determined by the pumping intensity. In our case the energy of the system is

$$E(n_1, n_2) = E_1 + E_2$$

where E_1 is the CTEs energy, and E_2 is the energy of the dissociated electrons and holes.

If the repulsion of excitons is taken into account their energy will be

$$E_1(n_1) = n_1 \Delta + E_{int}$$

where E_{int} is the energy of the repulsion of 2D CT excitons .If we introduce the lattice spacing a and a number of sites on interface

$$N = 1/a^2$$

then

$$E_{int} = N A \left(\frac{n_1}{N}\right)^{\frac{5}{2}}$$

where $A = 2\mu^2/a^3$

The expression used for E_{int} can be obtained if we take into account that the total energy of excitons interacting with one another (with the accuracy up to the factor of the order 1) equals

$$n_1 \cdot 2 \frac{\mu^2}{d^3} \sim n_1^{5/2}$$

where d is the average distance between CTEs

and $n_1 = N(a/d)^2 \sim \frac{1}{d^2}$

At the same time the energy of dissociated electrons and holes is

$E_2(n_2) = n_2(\Delta + B) + E\{kin\}(n_2)$

where B is the excess of the state of

the dissociated electron and hole over the CTE state and

$$E\{kin\}(n_{\ell}) = C\ n_{\ell}^{2}/N$$

The quadratic term in n_{ℓ} is the total kinetic energy of 2D electrons and holes in the ground state. Near the threshold this term carries in only small contribution to the total energy of electrons and holes.

Here we introduce the notation:

$$C = 2\pi^{2}\hbar^{2}/a^{2}m,$$

where $\hbar$ is the Plank constant and m is a mass of the free carriers (we neglect here the difference between m_e and m_h).

The total energy of the system at the fixed total number n of electron-hole pairs can be written as:

$$E(n_2) = N(\zeta B + C\zeta^2 + A(k - \xi)^{\frac{5}{2}}) +$$

$$+ \; k \cdot N \cdot \Delta,$$

where $\xi = n_2 / N$, $k = n / N$.

The derivative $\frac{d\,E(n_2)}{d\zeta}$ at $\zeta = 0$

is equal to:

$$\frac{dE}{d\zeta} = N\left(B - \frac{5}{2} A k^{\frac{3}{2}}\right)$$

For small k (weak pumping) this derivative is positive. It means that the minimum of total energy corresponds to

$$\zeta = 0$$

and free charges are absent. However, for

$$k > k_c$$

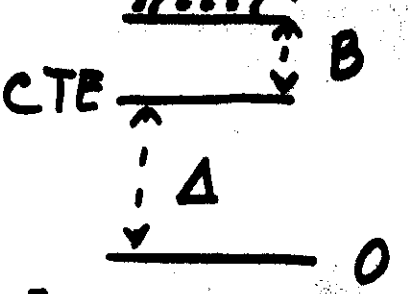
where k_c is some critical value of k_e :

$$k_c = (2B/5A)^{\frac{2}{3}},$$

the derivative of energy becomes ~~positive~~ negative

and a minimum of the energy $E(n_2)$

corresponds to some $\zeta_{min}(k) > 0$.



$$E_{tot}(n_2) =$$

$$= N\left[\zeta B + A(k-\zeta)^{5/2} + C\zeta^2\right] +$$

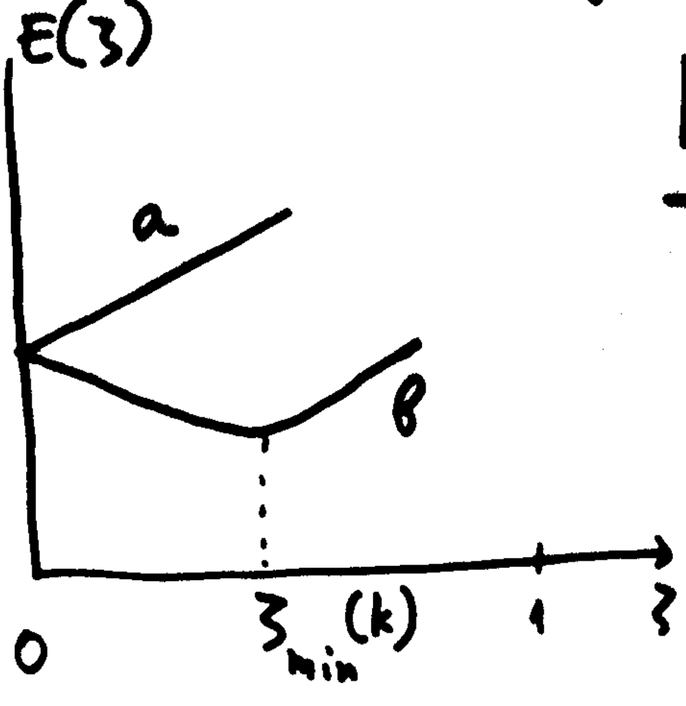
$$+ \kappa N \Delta$$

$\zeta = n_2/N$, $k = n/N$, $n_1 + n_2 = n$

$0 < \zeta < 1$, $A = \mu^2/a^3$, $C > 0$.

$$\frac{dE(\zeta)}{d\zeta} = N\left[B - \frac{5}{2}A(k-\zeta)^{3/2} + 2C\zeta\right]$$

At $\zeta = 0$: $\left.\frac{dE}{d\zeta}\right|_0 = N\left(B - \frac{5A}{2}k^{3/2}\right)$



$$\underline{k_c = \left(\frac{2B}{5A}\right)^{2/3}}$$

a) $k < k_c$, $\underline{\zeta_{min} = 0}$

b) $k > k_c$,

$\underline{\zeta_{min} > 0}$

Minimizing the energy $E(n_2)$ by ζ we find the equation for ζ_{min} :

$$B - \frac{5}{2} A (k-\zeta)^{\frac{3}{2}} + 2C\zeta = 0.$$

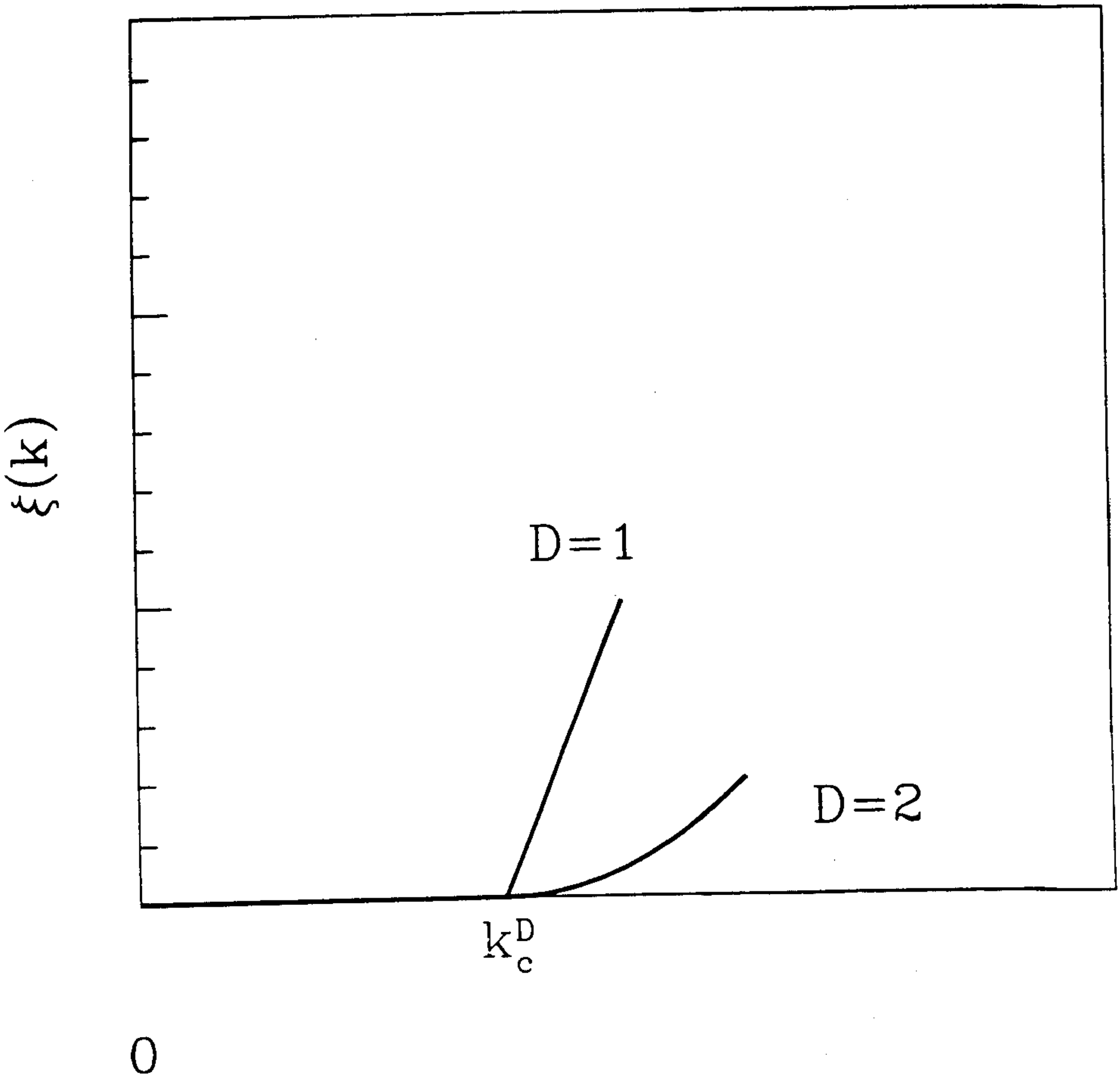
From these equation it follows that if

$$k > k_c ,$$

then near the threshold ζ varies in accordance with the linear law :

$$\zeta = (k - k_c)/\left(1 + \frac{4}{3} k_c (C/B)\right)$$

The appearance of free carriers at $k > k_c$ corresponds to transition into a conducting state.


ξ(k)
D=1
D=2
k_c^D
0

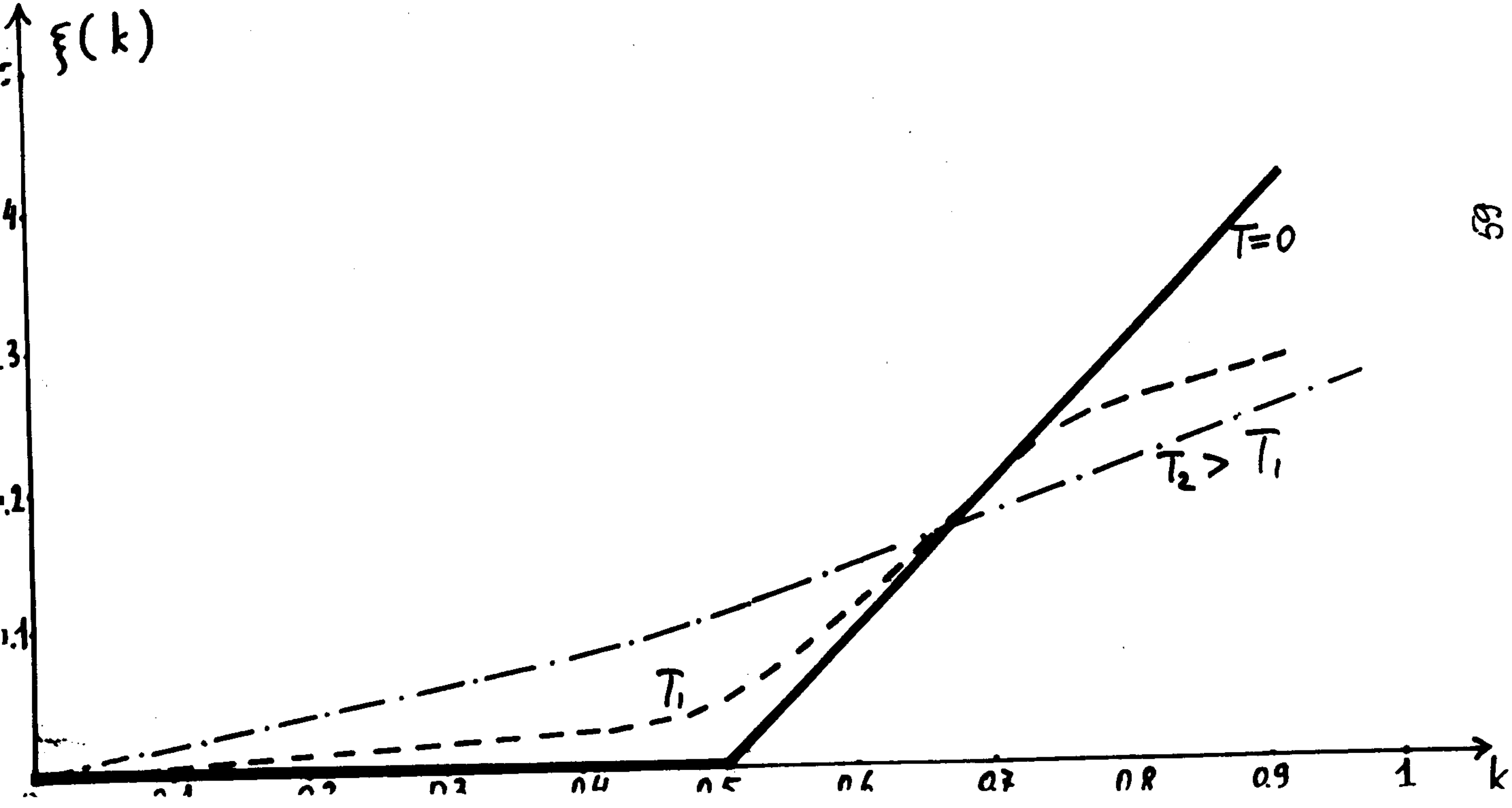
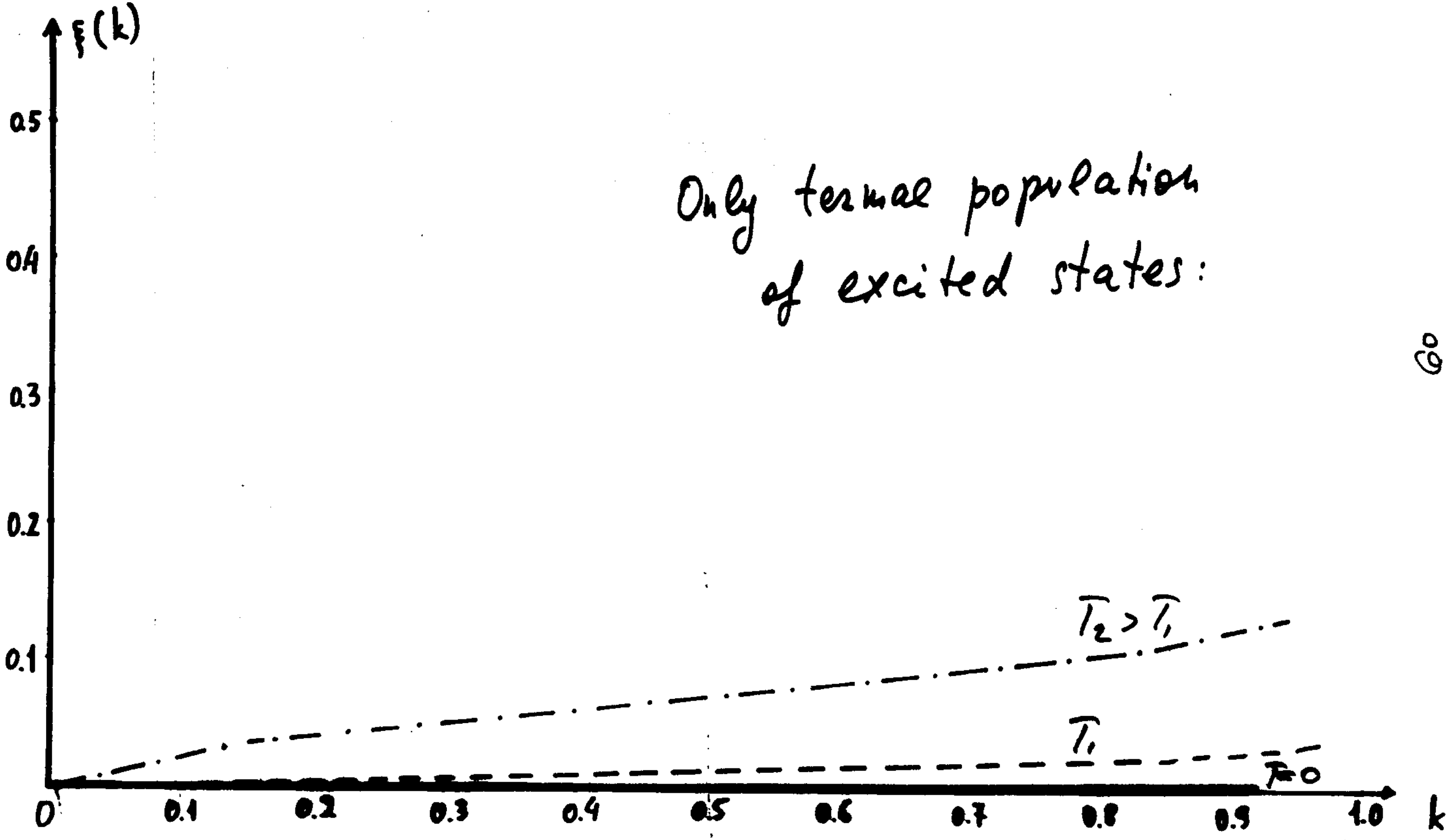


Fig. 2

Fig. 5



Only termal population
of excited states:

Discussion

Let us estimate, first of all, the CTE critical concentrations for which the transition we are discussing would take place. Making use of the relations obtained above, we have

$$k_c = (B\, a^3 / 2\mu^2)$$

Assuming, for example, B=0.1 eV, a=5A and μ =20D, which is not rare values for the case of CT excitons, we obtain

$$k_c \approx 0.1.$$

Thus, approximately 10 % of the molecules in the region of the interface should be in the excited state.

The account of the kinetic energy of the charges makes influence only on the dependence of charge carrier concentration on the pumping intensity n above the threshold: if we take into account this energy ζ varies near the threshold in accordance with the linear low.

$$n_2 = N\zeta = (n - Nk_c)/(1 + \frac{4}{3}k_c\frac{c}{B})$$

$$n_1 = n - n_2$$

The abovesaid only illustrates the main idea which, actually, requires clarification in many directions. One of the most interesting is the account of the nonequilibrium cluster structure of CTE distribution at short light pulse excitations of interface CT excitons. We can expect that in this case the repulsion induced appearence of free carriers can be observed in the measurements of photoconductivity at high intensity pumping.

Photovolt. cells with D-A interfaces

Short pulse pumping: clustering