united nations educational, scientific and cultural organization

international atomic energy agency

the
abdus salam
international centre for theoretical physics

SMR.1135 - 20

THIRD WORKSHOP ON
THIN FILMS PHYSICS AND TECHNOLOGY
(8 - 24 MARCH 1999)
including
TOPICAL CONFERENCE ON
MICROSTRUCTURE AND SURFACE MORPHOLOGY
EVOLUTION IN THIN FILMS
(24 - 26 MARCH 1999)

"Organic thin films for electronics and photonics"
Part II

Carlo TALIANI
Consiglio Nazionale delle Ricerche (C.N.R.)
Istituto di Spettroscopia Molecolare (I.S.M.)
Via Gobetti 101
40129 Bologna
ITALY

Film fabrication by O-MBD

- vacuum evaporation in high vacuum (HV) 10^{-7} torr and UHV ($\leq 10^{-10}$ torr)
  - growth rate 0.01 - 1 Å/s
  - several substrates (quartz, silicon, mica, HOPC, ITO, etc)

⇓

- molecularly ordered thin film
- layer by layer molecular growth

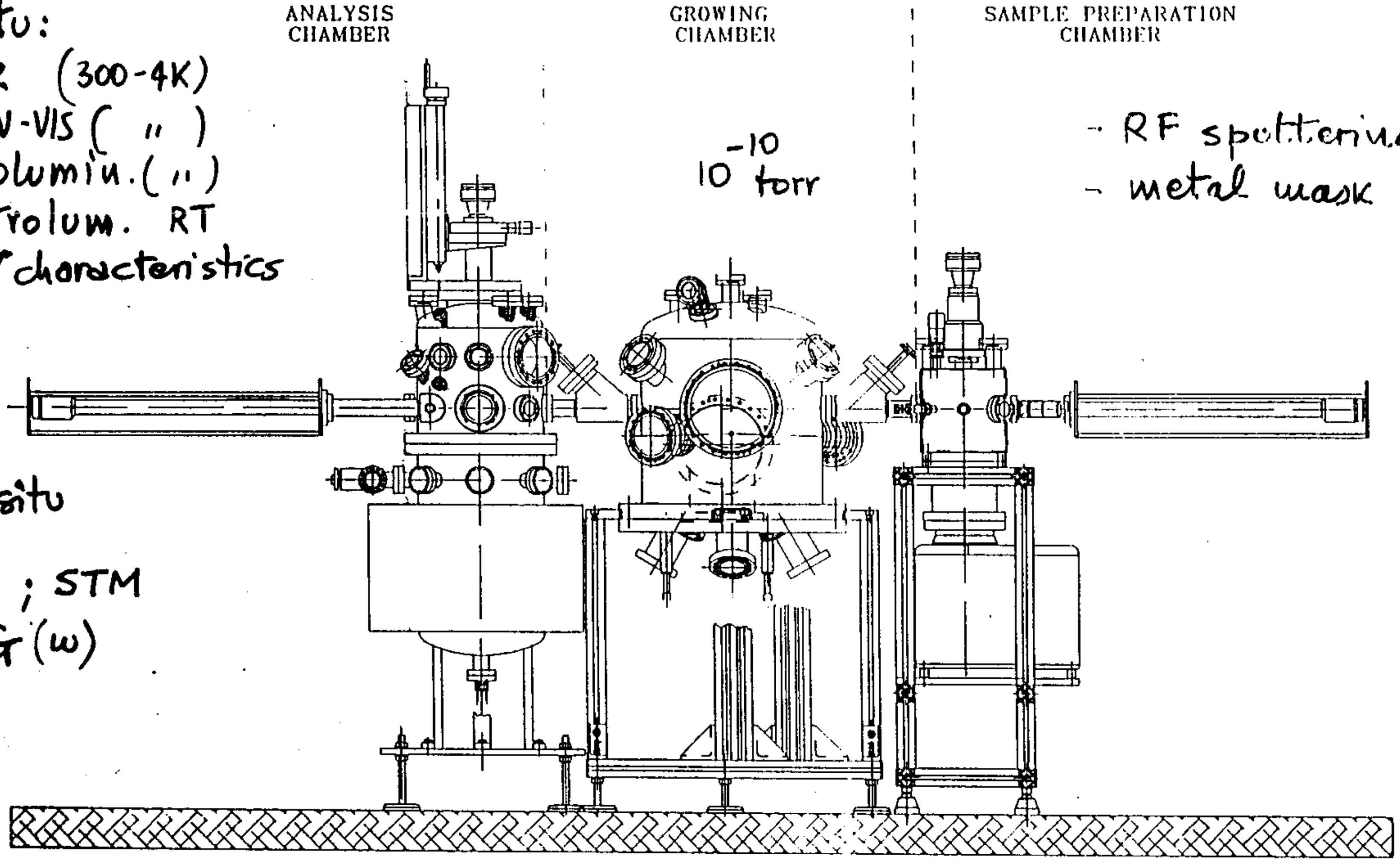
Goals

☐ control of the quality of:
  - the molecular orientation of the layer
  - definition of the interface
  - thickness of layers

☐ growth of devices in a clean environment

☐ characterization of devices "in situ".

in-situ:
- FT-IR (300-4K)
- NIR-UV-VIS (")
- photolumin. (")
- electrolum. RT
- I-V characteristics



10^{-10} torr

- RF sputtering
- metal mask evap.

ex-situ

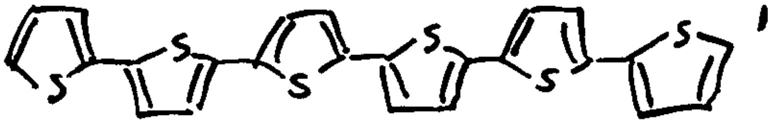
- AFM ; STM
- THG (ω)

- T_6
- C_{60}
- ZnPc
- Perylene
- ~~SiOx~~
- AD

Descrizione OMBE SYSTEM
GENERAL SYSTEM LAY-OUT
FRONT VIEW
SCALA 1:5
COLLI
18/12/03
XRIAL VACUUM
NUMERO DISEGNO Z000580 00

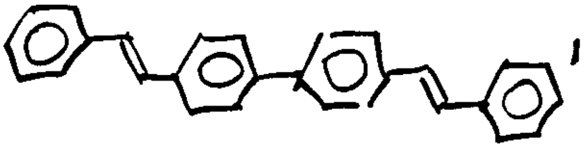
Materials

Ⓐ Organics

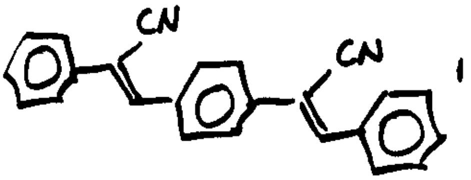
* 

T_6 , (T_4), (T_5

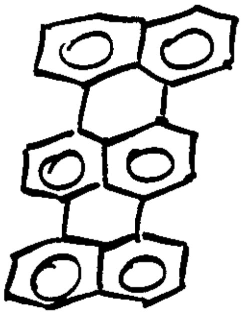
$T_6 d_n$



DSDP



3PPV CN



terrilene

* Fullerene C_{60} [2, 5, 6]

Fullerene C_{76} [2, 5, 1]

Fullerene C_{82}

* Phtalocyanines [4, 6]

* Perylenes [5, 6]

Catenanes [3]

Rotaxanes [4]

* presently loaded in UHV K-cells. (1997)

Ⓑ electrodes Al, Au, Ag

Ⓒ interface SiOx, fluorinated polymers.

1 TMR SELOA
2 TMR FULPROP
3 TMR ENBAC
4 TRM DRUM
5 JOULE-T. EUROSCI
6 BRITE-E MOLAC

☐ Rigid-Rod Conjugated Organic Semiconductors

- give rise to ordered thin films by evaporation
- morphology depends on evap. conditions :

substrate material, substrate temperature, base pressure, substrate angle, thickness...

access to → NEW ARCHITECTURES

☐ Processes (→ Devices).

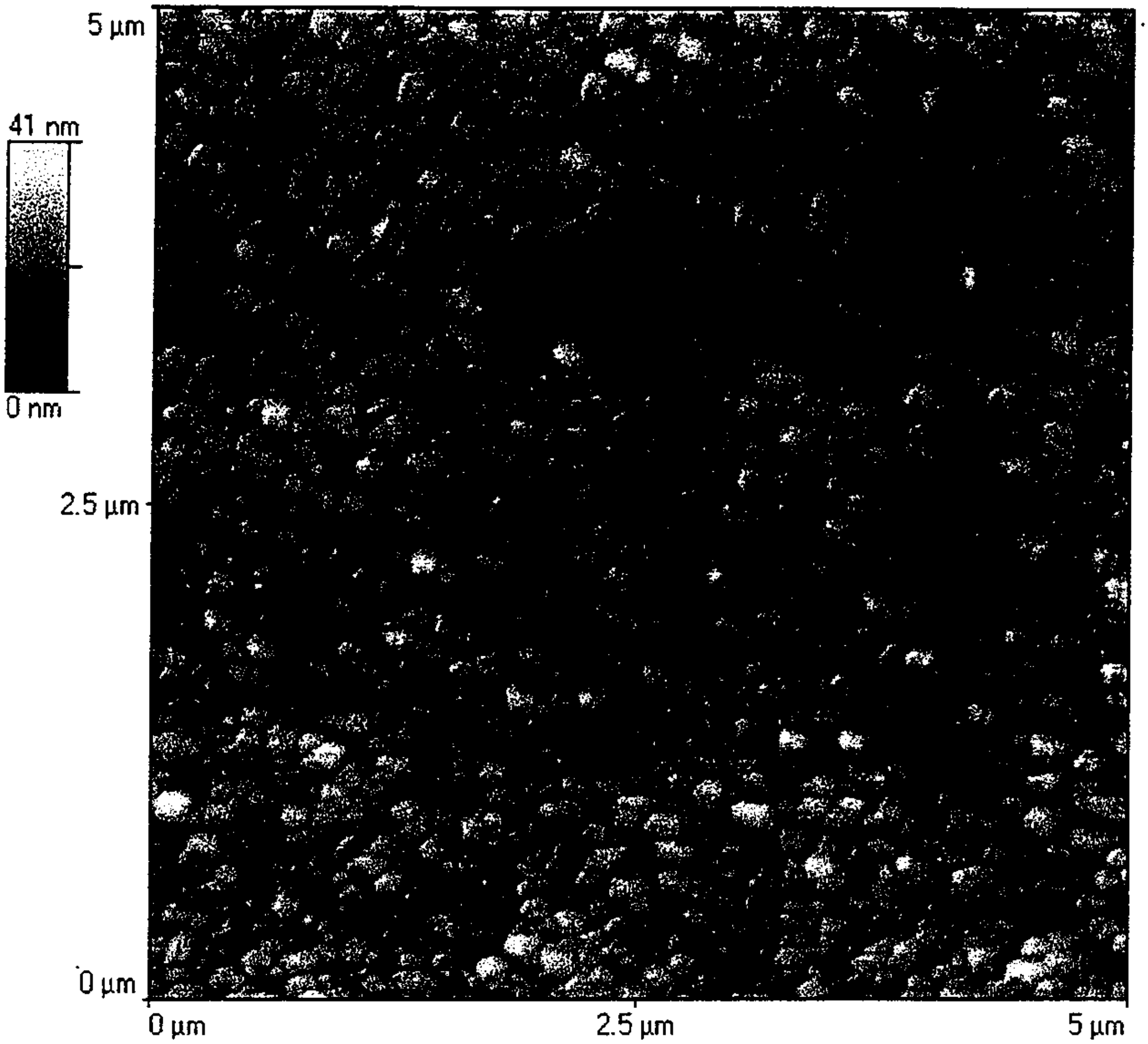
1) Charge injection → transport → recombination
↓
Emission ← Energy transport ← exciton formation
(Organic LED)

2) Photoinduced charge generation → separation
↓
transport
(Photovoltaic,
Photodetectors, SHG)

3) Photoind. charge gen. + NLO chromophore
↓
NL response due to Stark effect
(Photorefractivity)

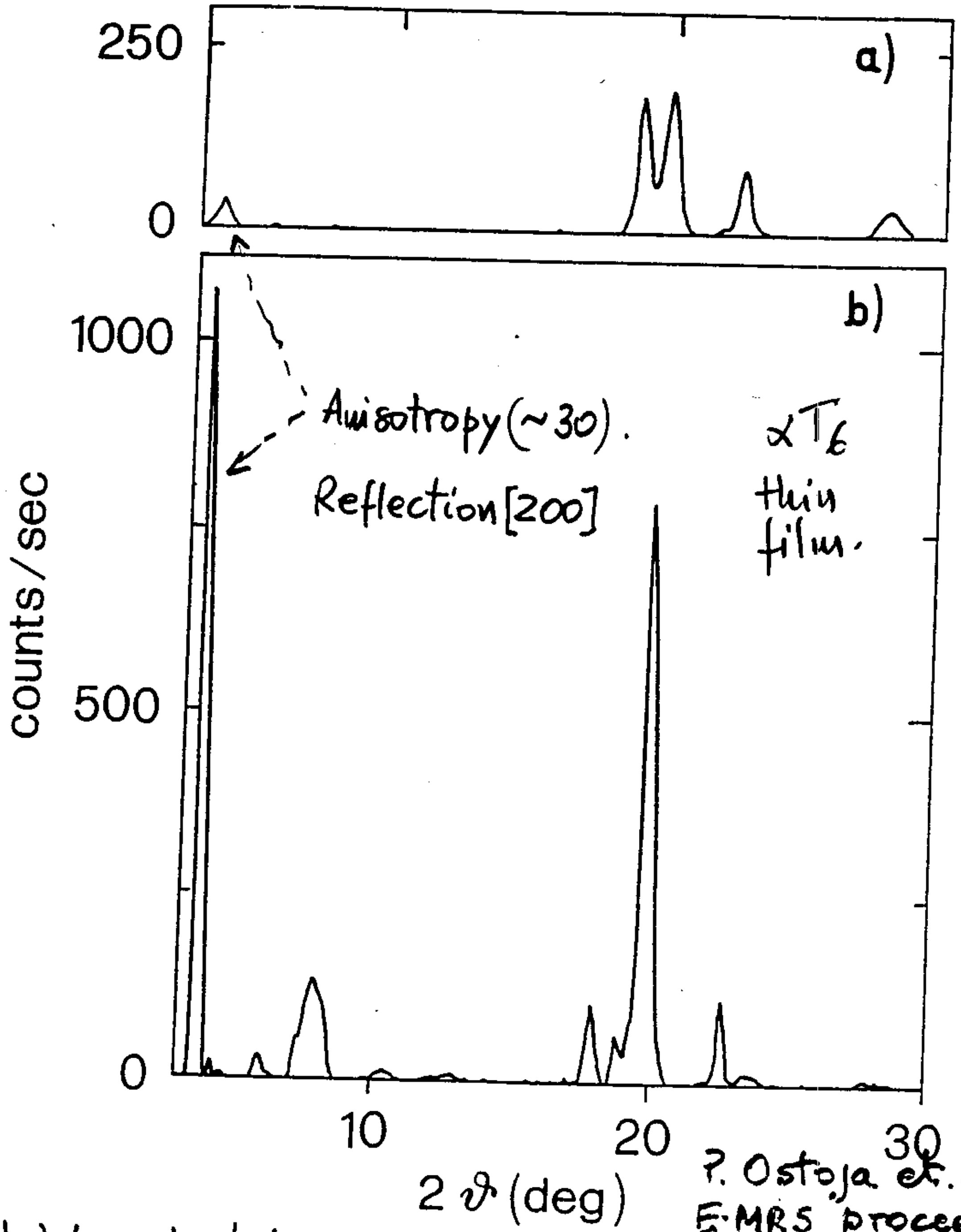
4) Photoinduced absorption
(Optical Limiting)

αT_6 Thin Film
Typical Morphology



grain diameter 200÷2000 nm
depending on $T_{subr.}$

GRAZING INCIDENCE X-RAY DIFFRACTION



Anisotropy (~30).
Reflection [200]

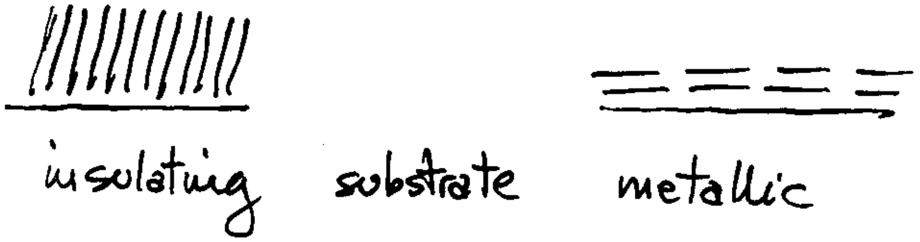
αT_6 thin film.

P. Ostoja et. al.
E-MRS proceed. June '9

- very high orientation – grain size ~ 30 nm.
- no appreciable amorphous phase.

X-ray diffraction patterns taken on an evaporated α-sexithienyl film at 0.5 deg grazing incidence (a) and symmetric Bragg-Brentano geometry (b). Note the anisotropy of the relative peak intensities in the two patterns.

- Rigid-rod conjugated organic semiconductors



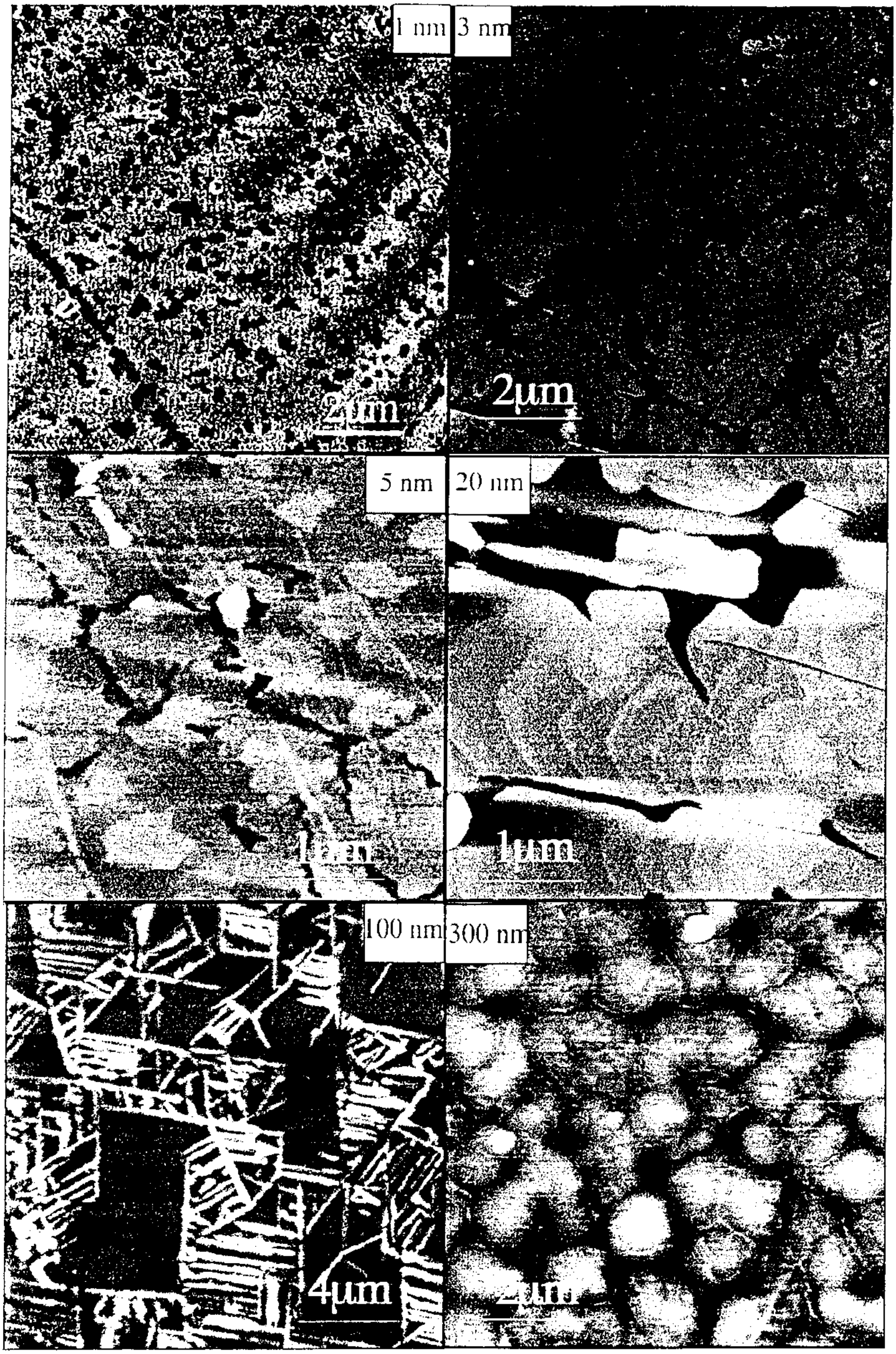
- Spherical conjugated semicon. fullerenes

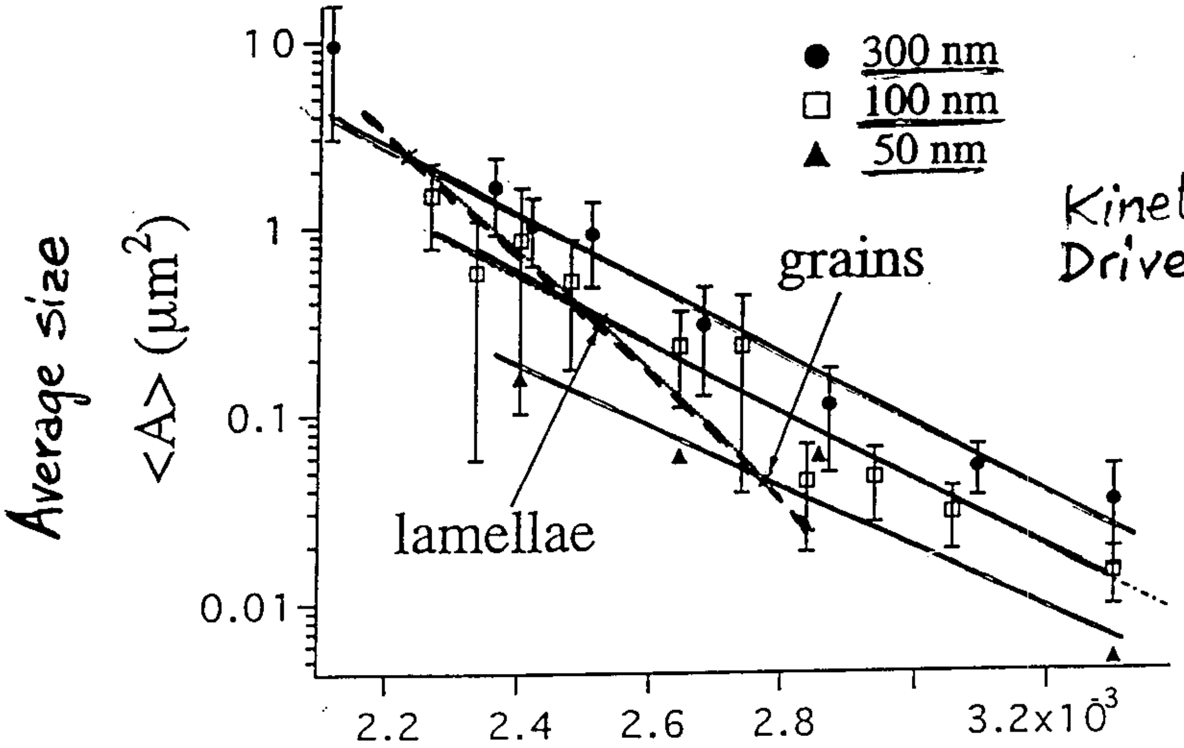
face centered cubic

Processes	Devices
charge injection transport recombination	OLED
exciton formation transport emission	
charge generation separation transport	Photovoltaic
Non-linear opt. response	Photorefractivity
excited state absorption	Optical limiting.


4µm
2µm

$T_{sub}=150°C$ αT_6 on mica

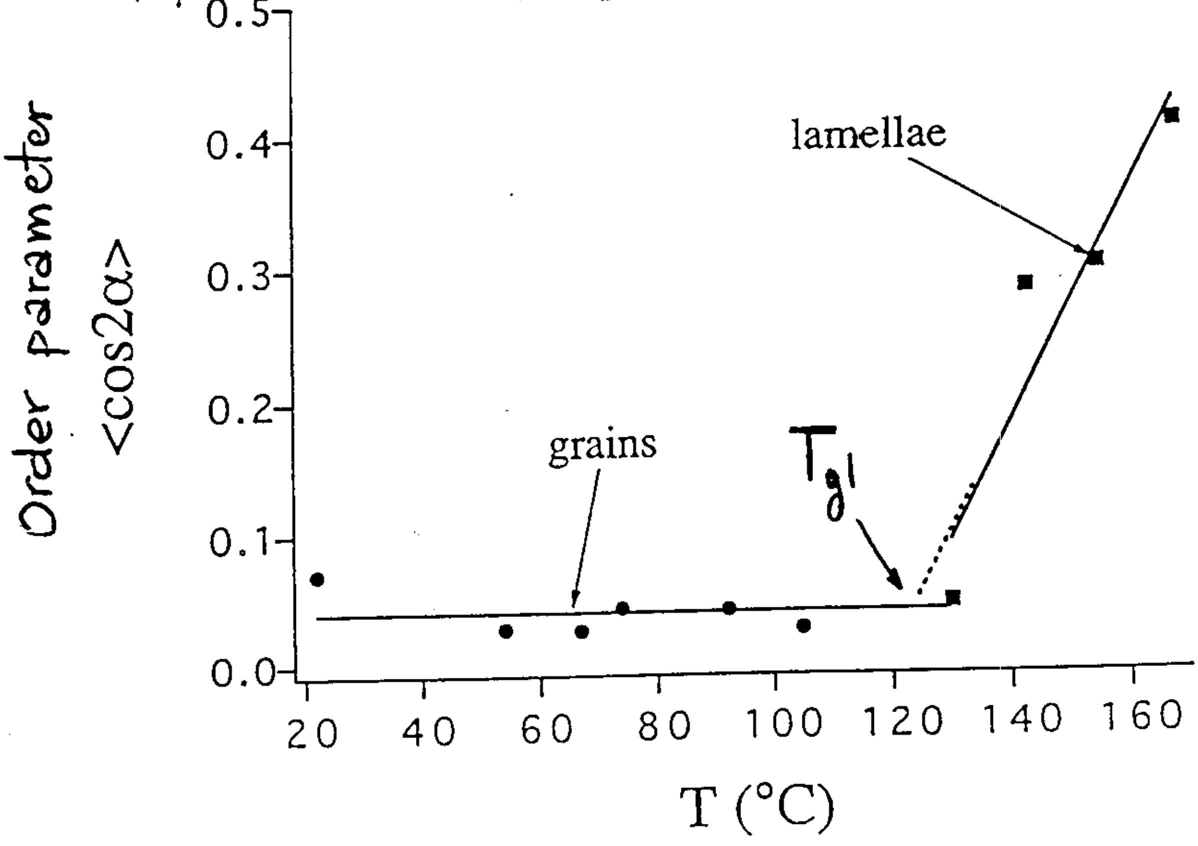




Kinetically Driven Growth

- Arrhenius plot
- grain → lamellae transition depends on thickness

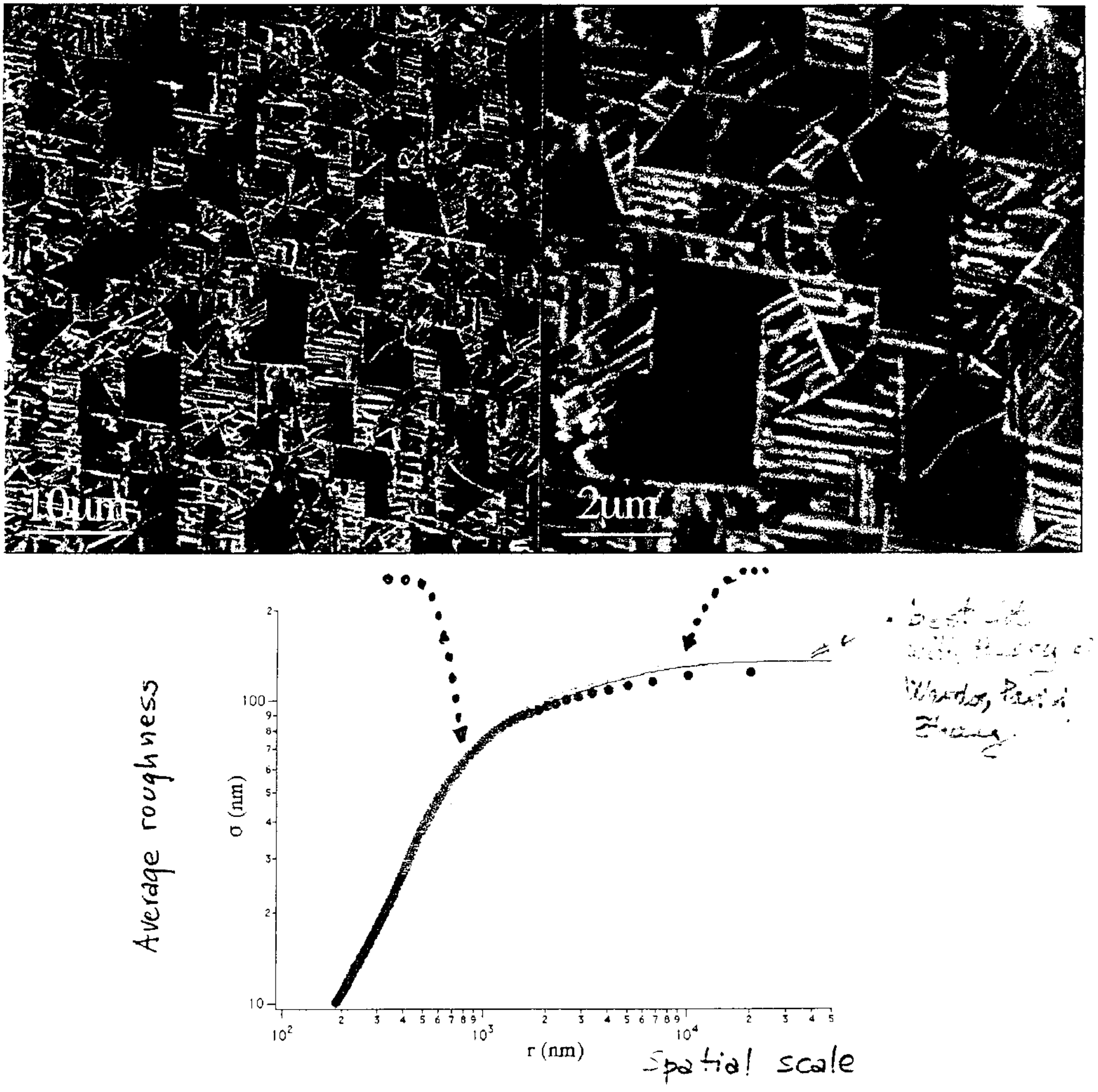
small $\xrightarrow{\Delta}$ larger grains depends on thickness



- Orientational ordering transition @ Tg'

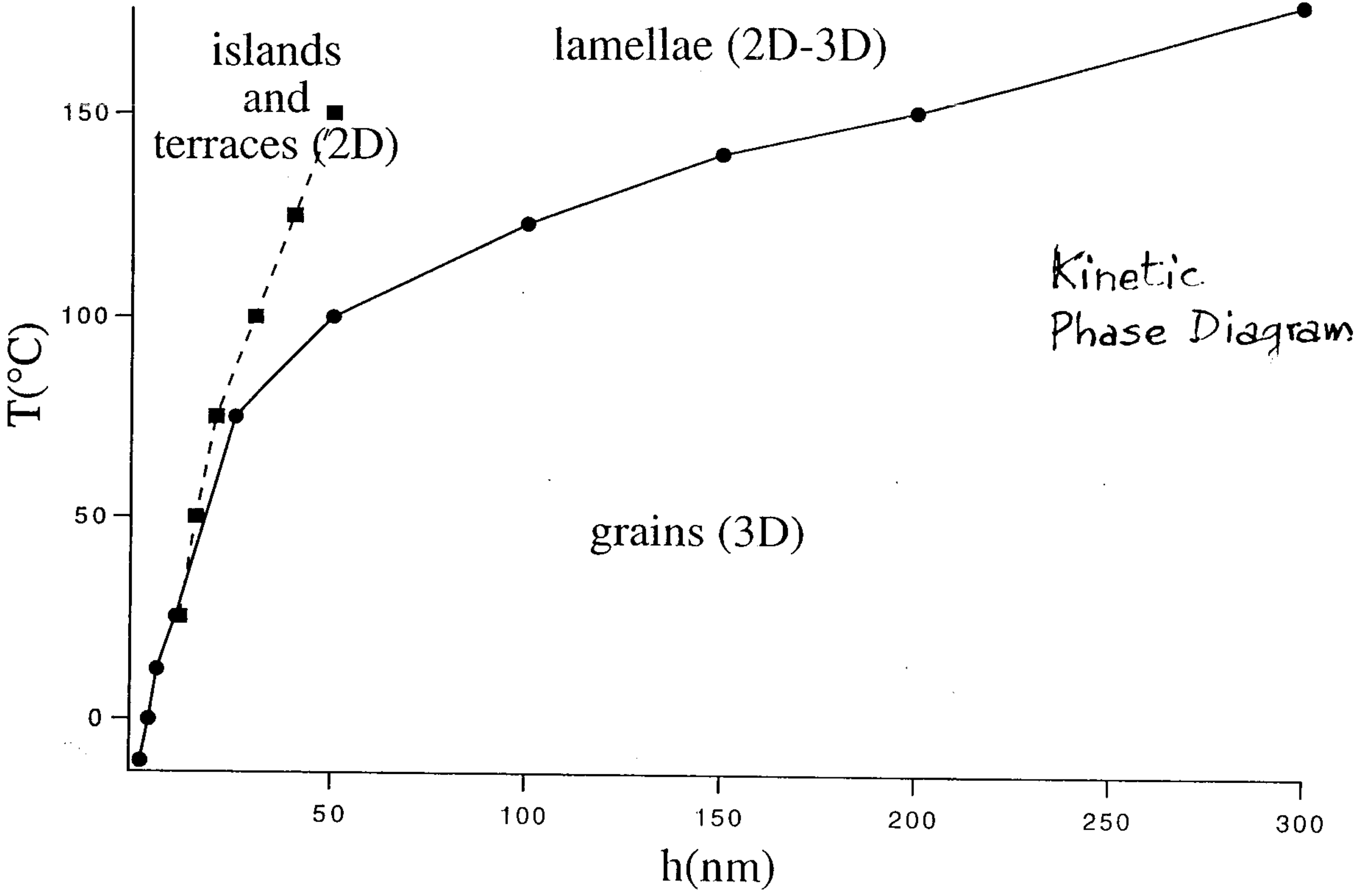
F. Biscarini et. al. Phys. Rev. B. 75, 52, 14868.

Roughness scaling properties

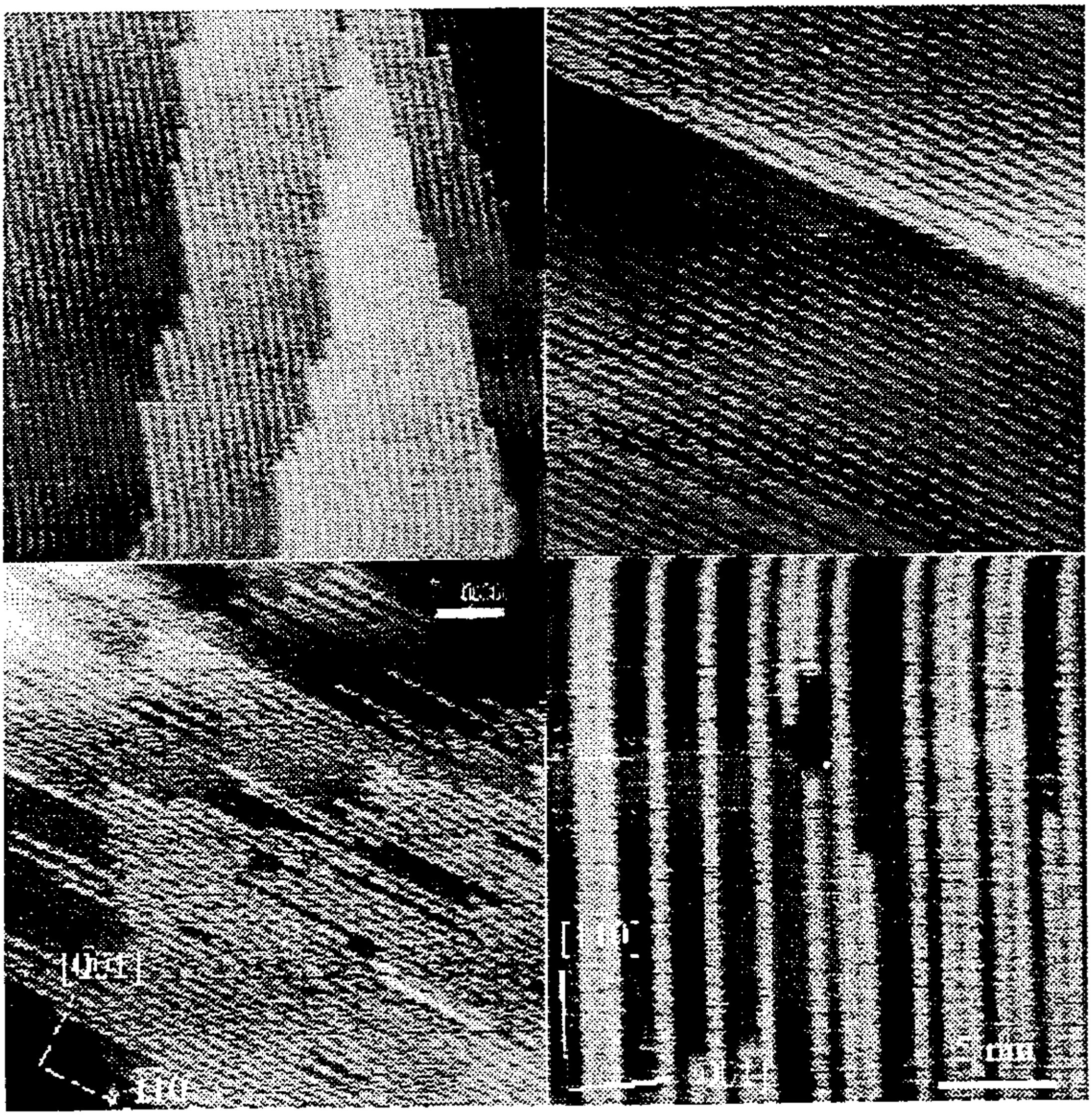


- Best fit with theory of [illegible], [illegible] Zhang.

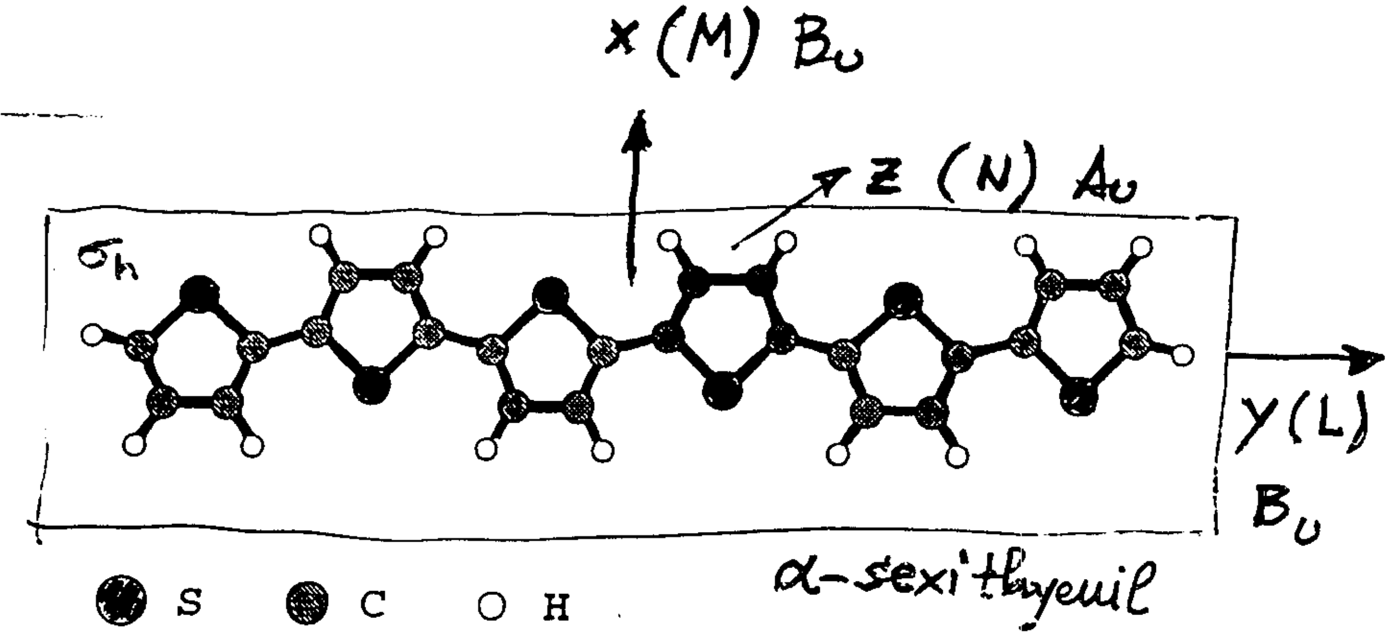
F. Biscarini et.al. Phys. Rev. Lett. 78, 2389 (97)


islands
and
terraces (2D)
lamellae (2D-3D)
Kinetic
Phase Diagram
grains (3D)
T(°C)
150
100
50
0
50
100
150
200
250
300
h(nm)

T6 on Au (110) - 1x2 reconstructed



L. Floreano et al. (19



α-sexithyenil

$\mathscr{C}_{2h}$	E	C_2	i	σ_h		
A_g	1	1	1	1	R_z	$\alpha_{xx}, \alpha_{yy}, \alpha_{zz}, \alpha_{xy}$
B_g	1	-1	1	-1	R_x, R_y	α_{yz}, α_{zz}
A_u	1	1	-1	-1	T_z	} dipole allowed transitions.
B_u	1	-1	-1	1	T_x, T_y	

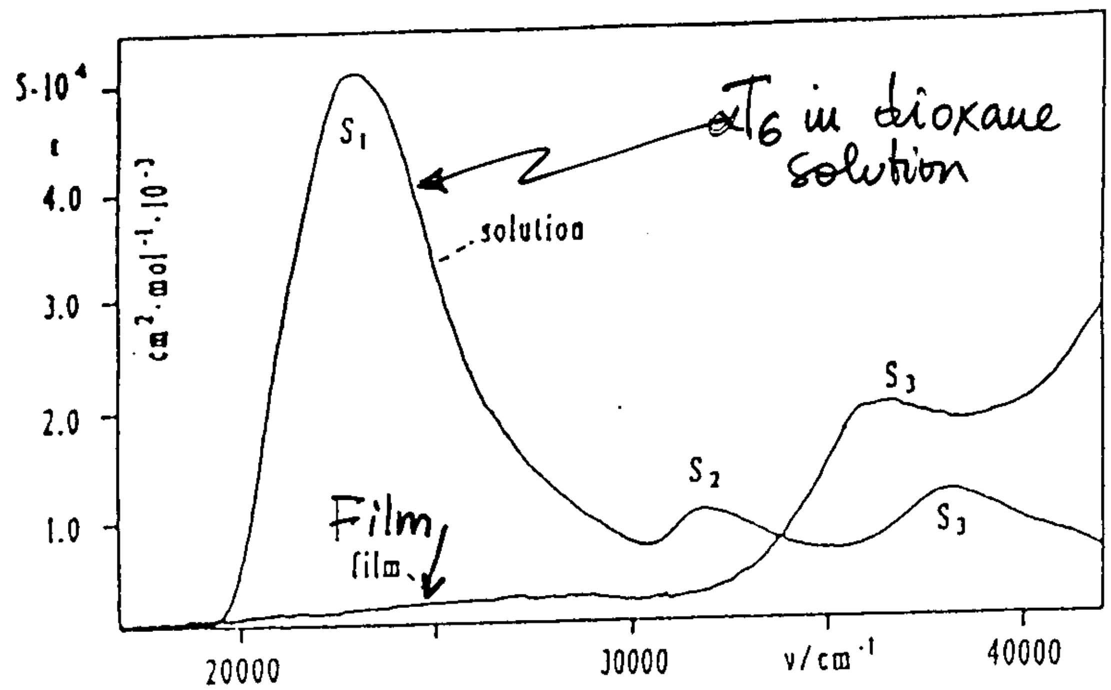


Fig. 3. Absorption spectra of 6T in solution (dioxane) and in a 2.2 nm film vapour deposited onto fused silica (surface normal parallel to incident beam).

D. Oelkrug et. al.

R. Colditz et. al.
Chem. Phys. 201, 309 (95)

5T		6T		
ΔE (eV)	symmetry	ΔE (eV)	symmetry	
2.53	$1\,^1B_2$	2.45	$1\,^1B_u$	L axis
3.35	$2\,^1A_1$	3.12	$2\,^1A_g$	
3.64	$3\,^1A_1$	3.57	$3\,^1A_g$	
3.93	$2\,^1B_2$	3.71	$2\,^1B_u$	M axis
4.33	$4\,^1A_1$	4.05	$3\,^1B_u$	
4.34	$3\,^1B_2$	4.13	$4\,^1A_g$	
4.82	$5\,^1A_1$	4.44	$4\,^1B_u$	
4.84	$4\,^1B_2$	4.62	$5\,^1A_g$	
4.91	$6\,^1A_1$	4.65	$5\,^1B_u$	
4.92	$5\,^1B_2$	4.85	$6\,^1B_u$	

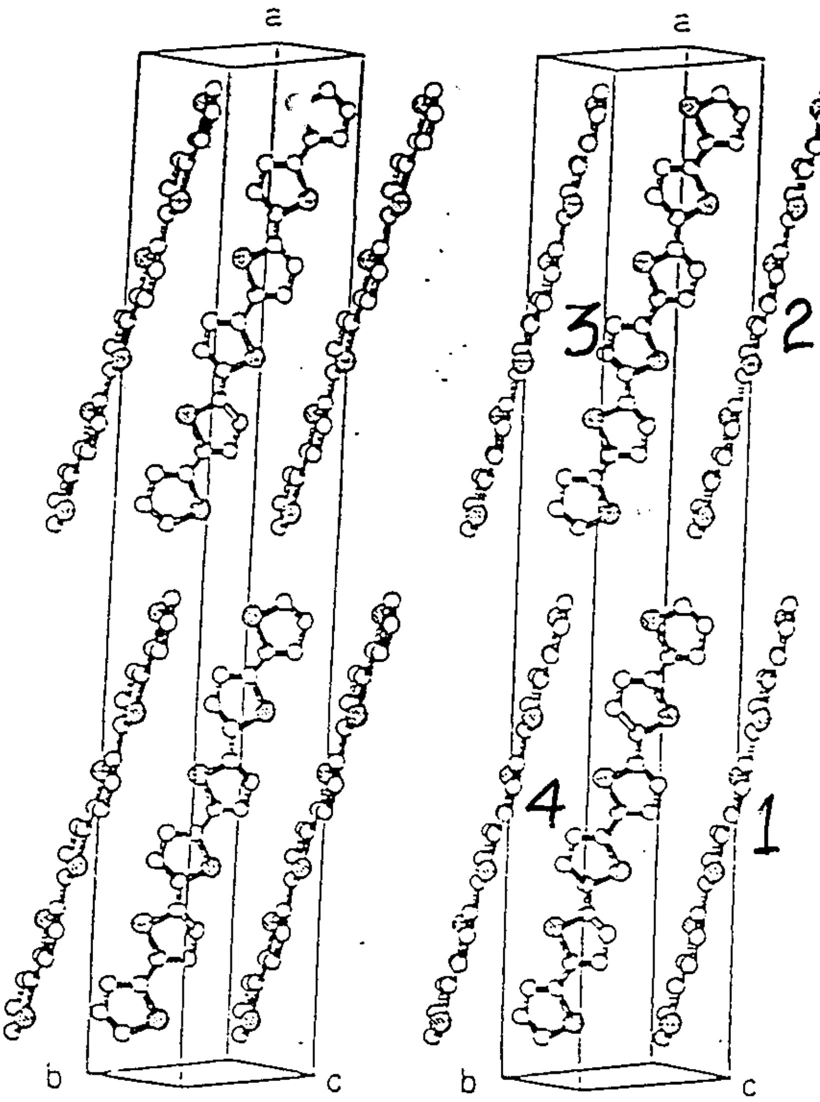
⇑

). Beljonne et. al.
~('97)

ble 2: INDO/MRD-CI singlet-singlet $S_0\rightarrow S_1$, singlet-triplet $S_0\rightarrow T_1$, and triplet-triplet $T_1\rightarrow T_n$ energies, calculated on the basis of the ground-state geometries of oligothiophenes. perimental data taken from optical measurements in solution are also included. All the ergies are given in eV.

⇓

		Th2	Th3	Th4	Th5	Th6	Th7	Th9	Th11
$S_0\rightarrow S_1$	Calc.	4.23	3.58	3.16	2.92	2.72			
	Exp.	4.12[a]	3.49[a]	3.18[a]	3.00[a]	2.72[b]	2.58[b]	2.45[b]	2.40[b]
$T_1\rightarrow T_n$	Calc.	4.37	3.42	3.01	2.62	2.40			
	Exp.		2.70[c]	2.21[c]		1.75[b]	1.60[b]	1.52[b]	1.45[b]
$S_0\rightarrow T_1$	Calc.	1.84	1.68	1.61	1.61	1.65			
	Exp.		1.74[d]						



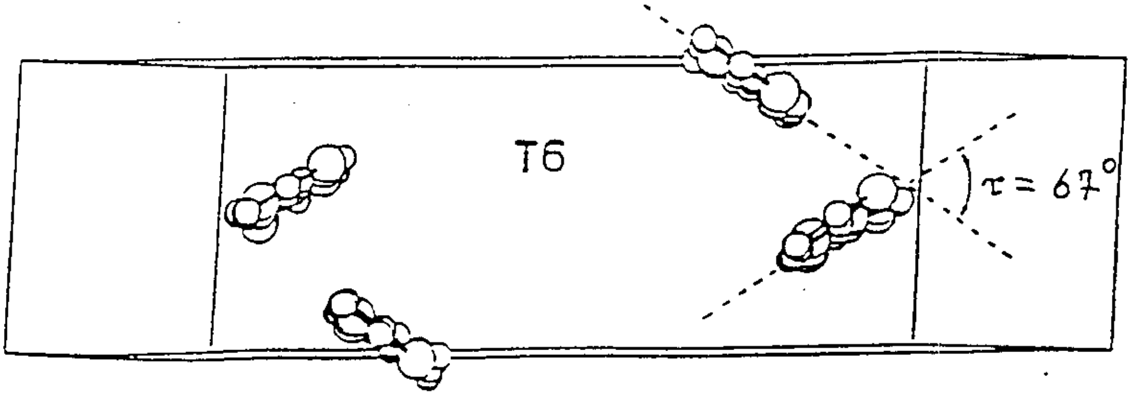
crystal system	monoclinic
space group	$P2_1/n$
Z	4
a (Å)	44.708
b (Å)	7.851
c (Å)	6.029
α (deg)	90.0
β (deg)	90.76
γ (deg)	90.0

$E(1) = 1$

$i(1) = 2$

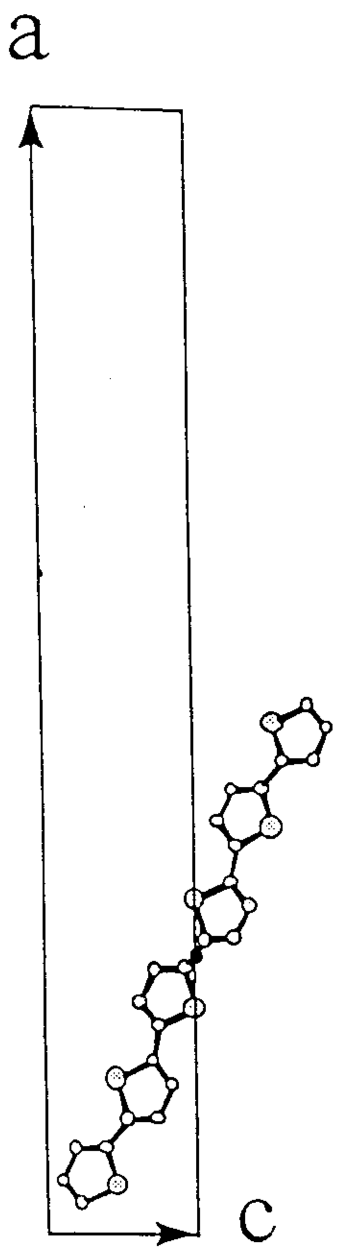
$\sigma_h(1) = 4$

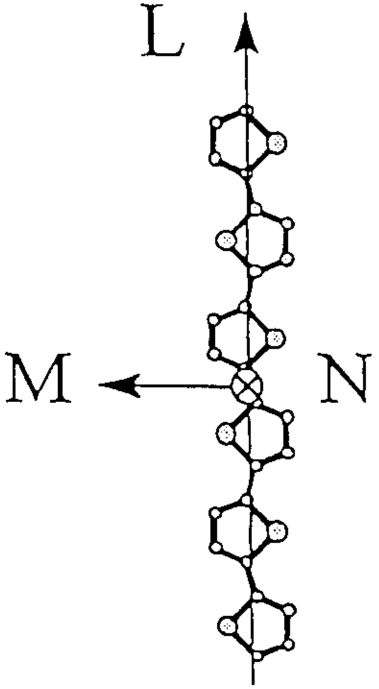
$C_2(1) = 3$

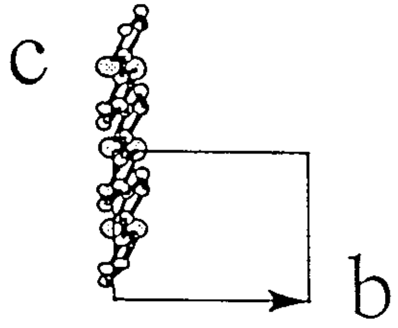


G. Horowitz et al. *Chem. Mat.* 7 (1995) 1337

W. Porzio et al. Acta Polymer. 44 (1993) 266.

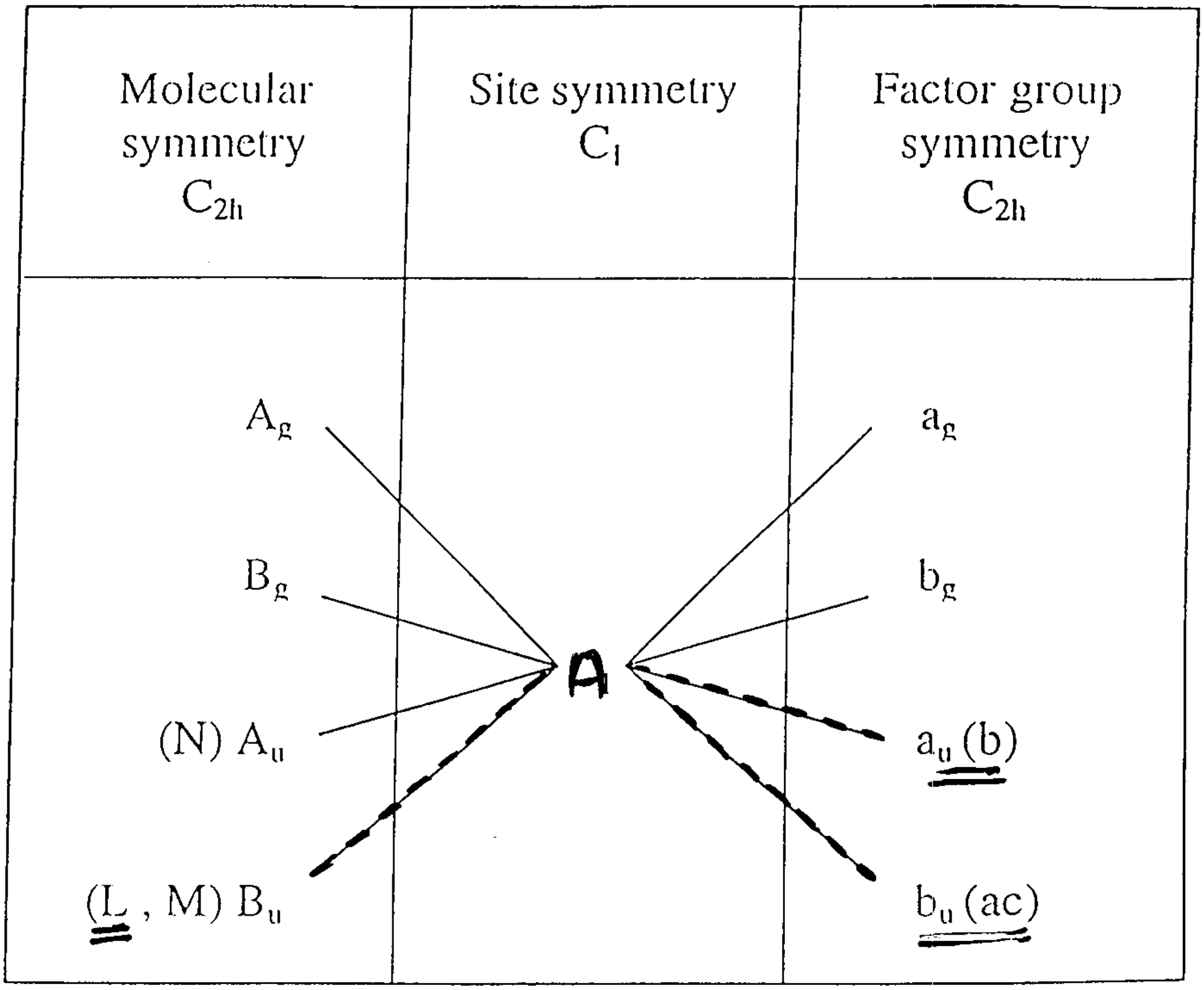

a
c


L
M
N


c
b

Correlation of Excited Electronic States of αT_6

Free Molecule ← in → Crystal

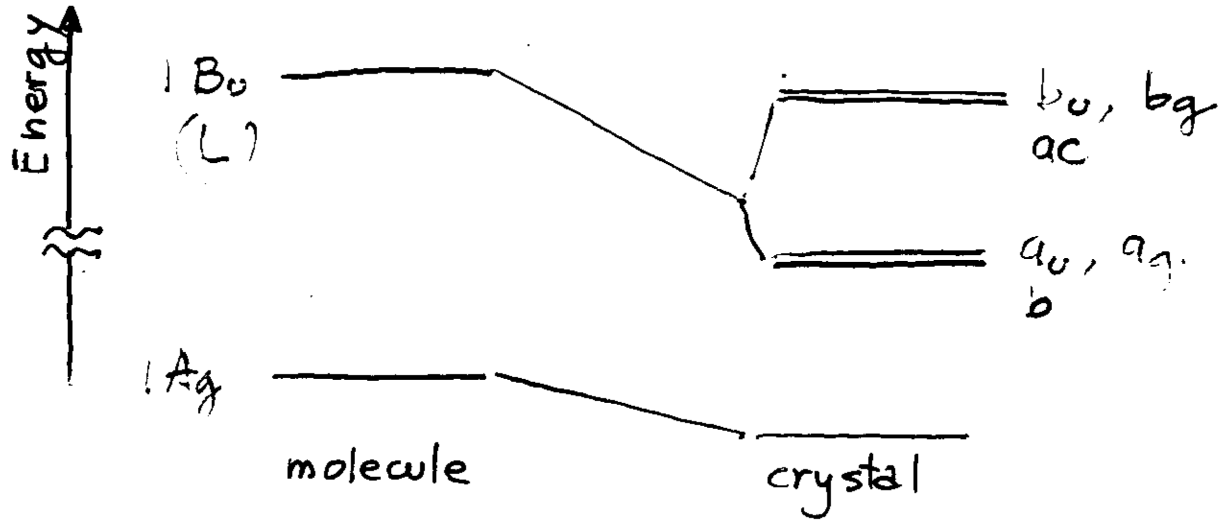


$$\begin{array}{lllllll}
E_{a_g}(k=0) = & E_0 - D & + I_{11} & + I_{12} & + I_{13} & + I_{14} \\
E_{b_g}(k=0) = & E_0 - D & + & + & - & - \\
E_{a_u}(k=0) = & E_0 - D & + & - & - & + \\
E_{b_u}(k=0) = & E_0 - D & + & - & + & -
\end{array}$$

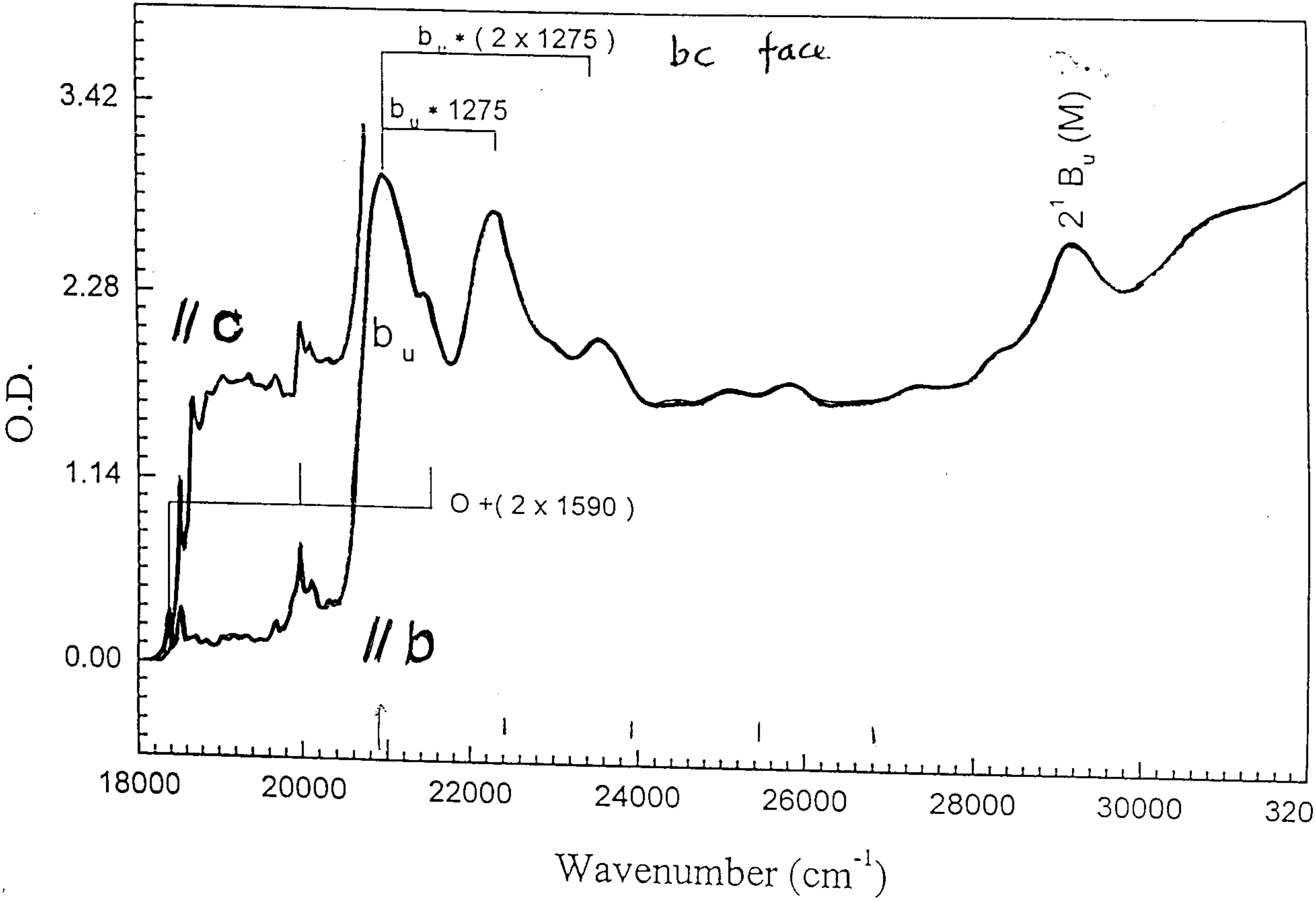
E_0 = electronic energy of the free molecule

D = difference of stabilization E in the excited and in the ground state Crystal Shift

$$I_{ij} = \sum_{n \neq m} \langle \varphi_n^* \varphi_m | V_{nm} | \varphi_n \varphi_m^* \rangle$$ Resonance Integrals

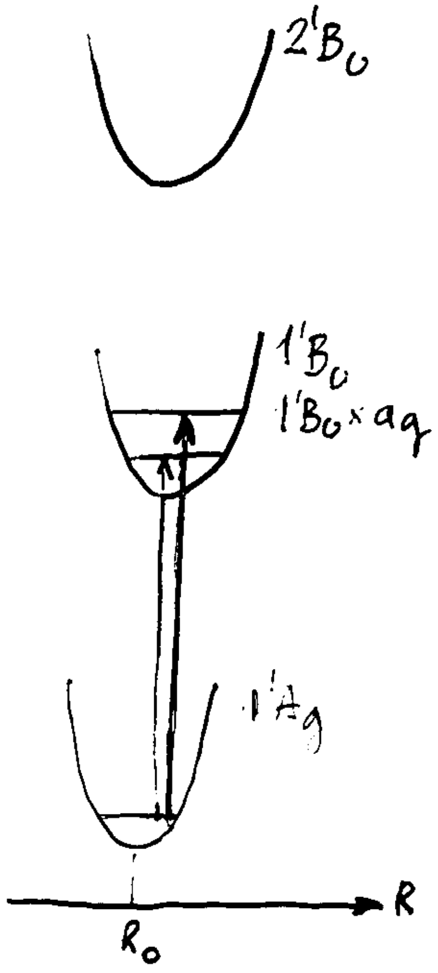


αT6 single crystal pol. absorbtion at 4.2K



M. Muccini
et. al.
J.C.P.
(to appear

Herzberg-Teller coupling in αT_6 - A special case



a_g modes couple 1^1B_u with 2^1B_u

—— $\langle 1A_g|\mu_y|1^1B_u\rangle$

—— $\langle 1A_g|\mu_y|1^1B_u\, a_g\rangle$

\+

Franck-Condon

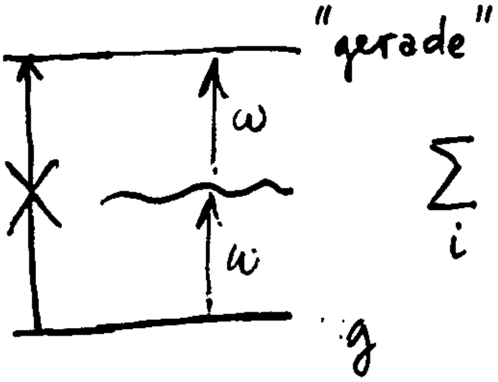
→ vibrational wf overlap $\langle 0|a_g\rangle_{FC}$

Herzberg-Teller

→ borrowing intensity from higher 2^1B_u state.

$$\rightarrow \langle 1^1A_g|\mu_y|1^1B_u\, a_g\rangle_{HT} = \sum_{\substack{n^1B_u \\ (n\neq 1)}} \frac{\langle 1^1A_g|\mu_x|n^1B_u\rangle}{\Delta E_{(nB_u-1B_u)}}$$

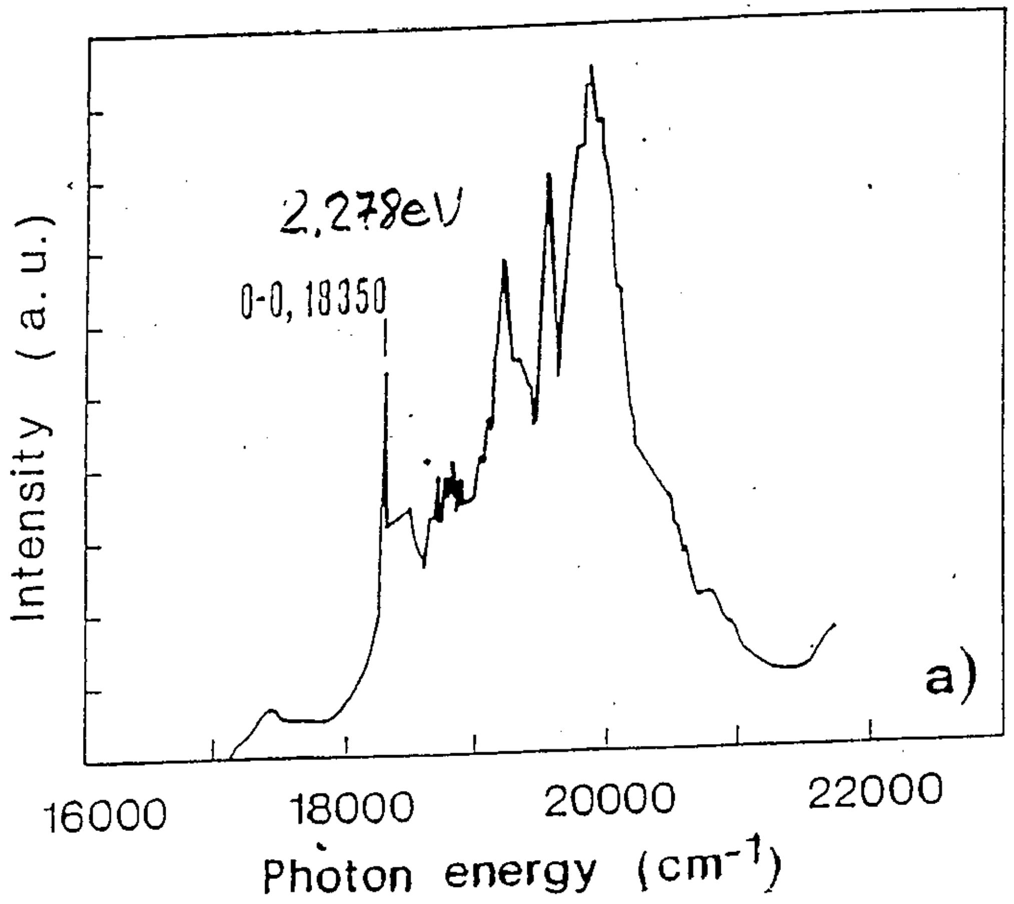
Two-photon absorption



$$\sum_i \frac{\langle g|er_1|u_i\rangle\langle u_i|er_2|g'\rangle}{E_i-\omega} \neq$$

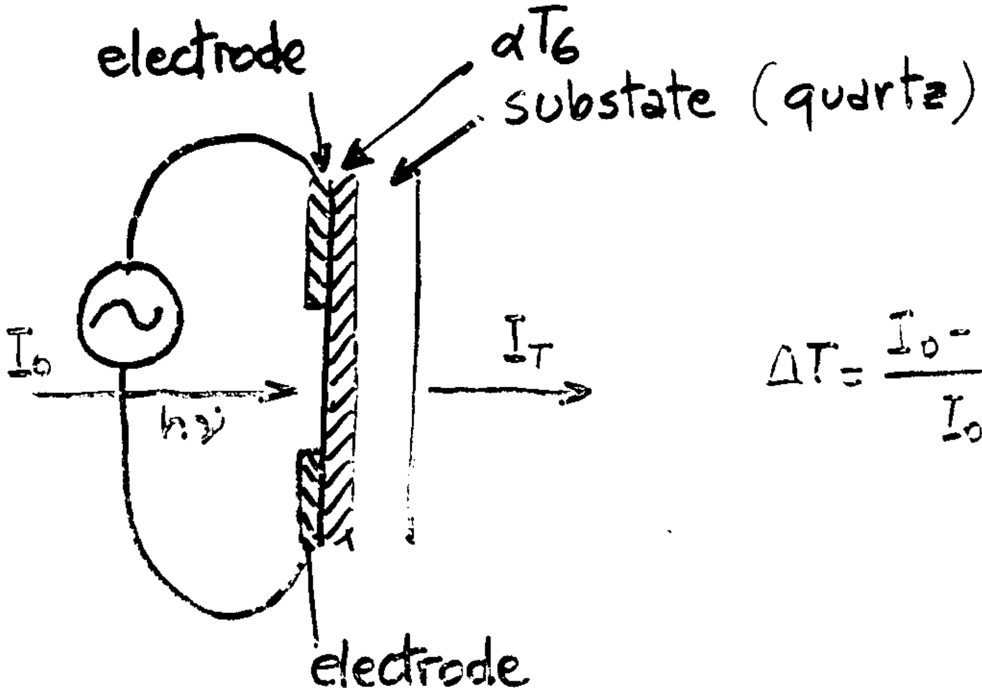
$g \otimes u \otimes g \not\subset g$

$g \otimes u \otimes u \subset g$

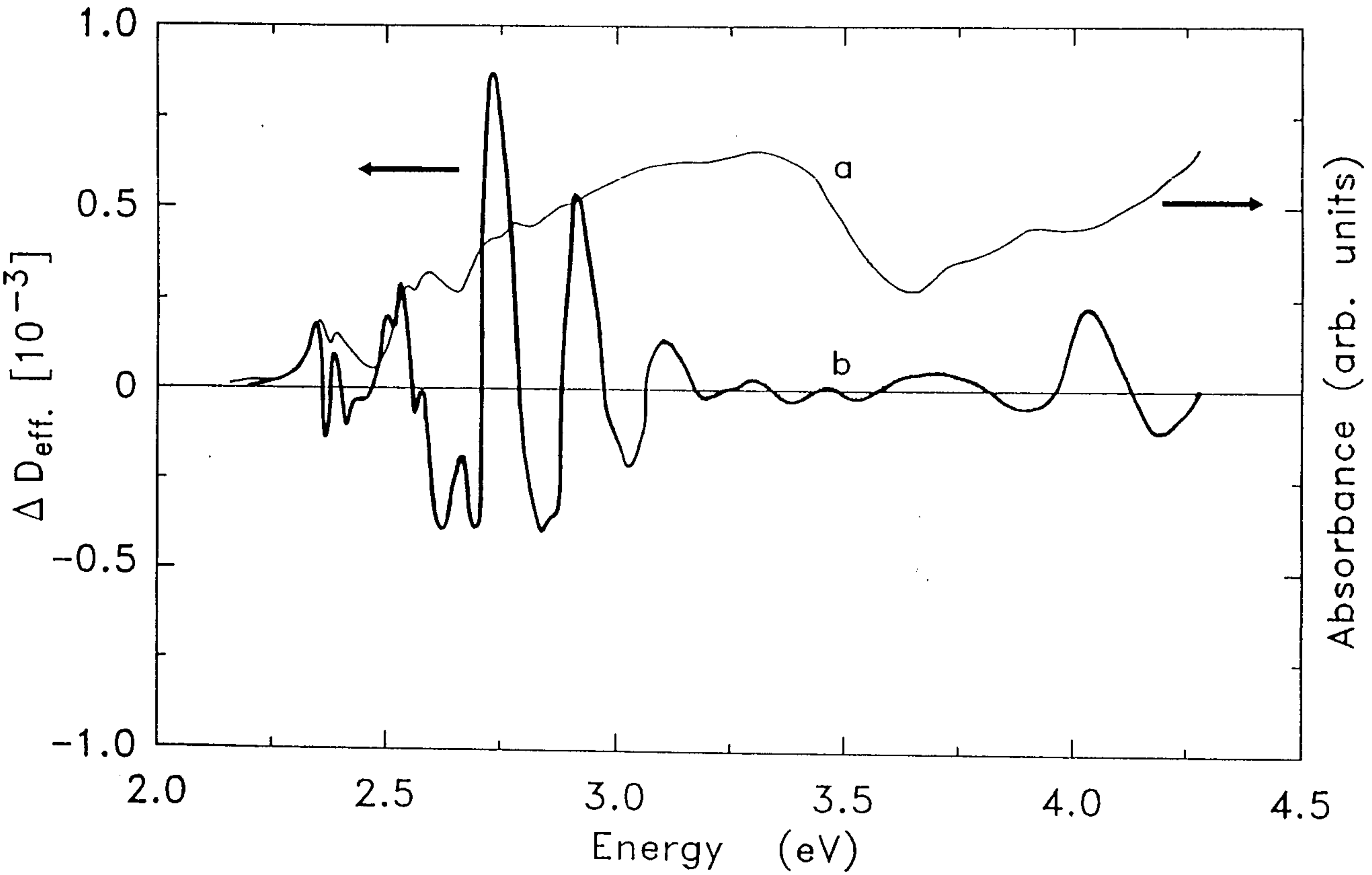


N. Periasamy, R. Danieli, G. Ruani, R. Zamboni, and C. Taliani, Phys. Rev. Lett. ,**68** (1992) 919

Electroabsorption



$$\Delta T = \frac{I_0 - I_T}{I_0}$$



1.0
0.5
0
−0.5
−1.0
$\Delta D_{\text{eff.}}\ [10^{-3}]$
a
b
2.0
2.5
3.0
3.5
4.0
4.5
Energy (eV)
Absorbance (arb. units)

Stark Shift

$$\Delta E = \Delta\mu \, F + \frac{1}{2} \Delta\alpha \, F^2$$ F = el. field

dip. mom. $\Delta\mu = \mu_e - \mu_g$ excited state
ground "

polariz. $\Delta\alpha = \alpha_e - \alpha_g$

→ For neutral excitations (Frenkel) $\Delta\mu = 0 \rightarrow \Delta E \propto F$

→ " charged " (CTE, → CB) $\Delta\mu \neq 0 \rightarrow \Delta E \propto F$

$$\left(\frac{\Delta I}{I}\right) = \frac{1}{\sqrt{2}} F_{eff.}^2 \left(\frac{\Delta\alpha}{2hc} \frac{\partial D}{\partial \nu} + \frac{\Delta\mu^2}{10 h^2 c^2} \frac{\partial^2 D}{\partial \nu^2}\right) \text{(from Liptay)}$$

$$\Downarrow$$

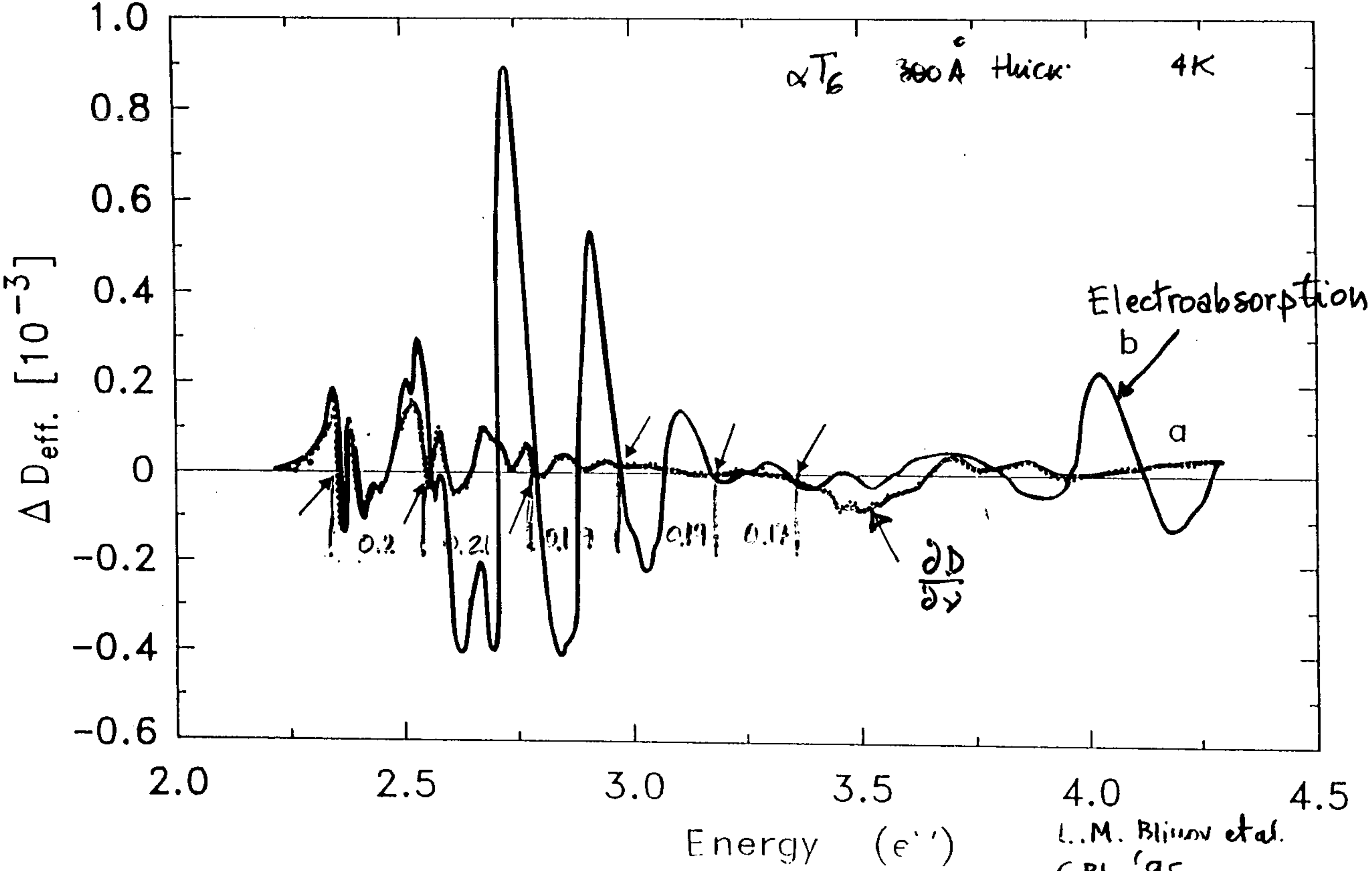
⟹ for Frenkel excitons $= 0$

i.e.

$$\frac{\Delta I}{I} = \frac{1}{\sqrt{2}} F_{eff.}^2 \frac{\Delta\alpha}{2hc} \frac{\partial D}{\partial \nu}$$

⟹ for Charge transfer excitons

$$\frac{\Delta I}{I} \sim A \frac{\partial D}{\partial \nu} + B \frac{\partial^2 D}{\partial \nu^2}$$



L.M. Blinov et al.
CPL '95