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I.C.T.P., P.O. BOX 586, 34100 TRIESTE, ITALY, CABLE: CENTRATOM TRIESTE

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AND SELF-ORGANIZING NANOSTRUCTURES
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"Light Emission from Porous Silicon: Recent Theoretical Results"

M.J. CALDAS
Universidade de Sao Paulo
Centro de Computacao Eletronica
Av. Prof. Luciano Gualberto
Tr 3. No. 71, Cidade Universitaria
05508-900 Sao Paulo
BRAZIL

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

Light emission from porous Silicon: Recent theoretical results

Marília Junqueira Caldas

Instituto de Física
Universidade de São Paulo
Brasil

R. Baierle, IF-USP
S. Ossicini, INFM & DF-UNIMO
E. Molinari, INFM & DF-UNIMO

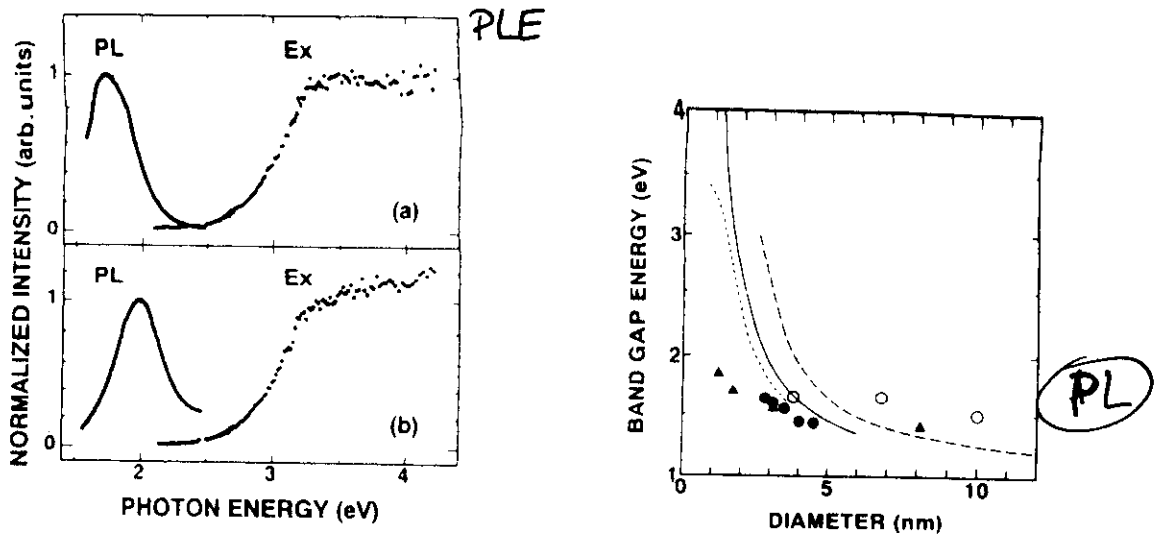
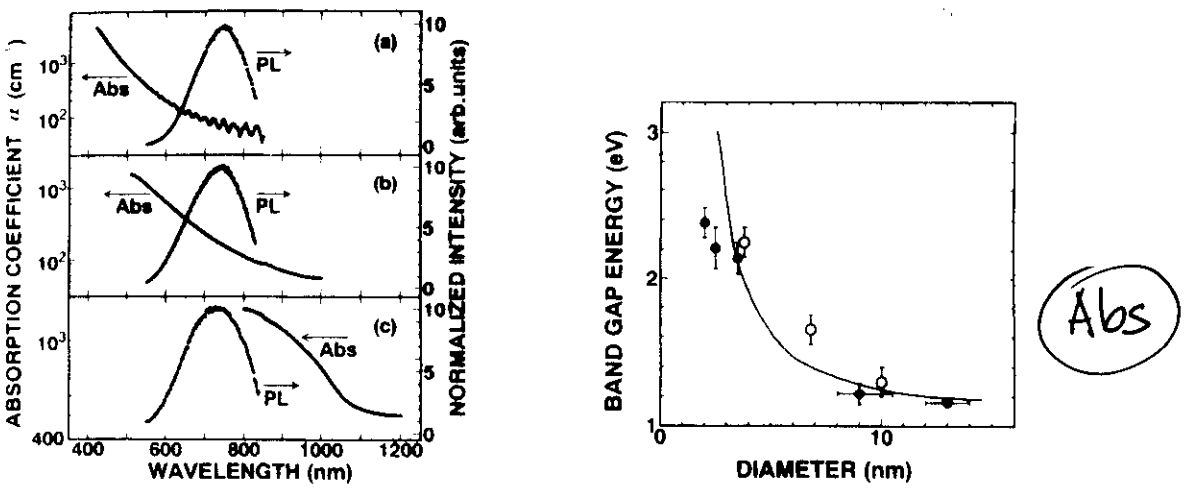


Fig. 3.3. Photoluminescence and photoluminescence excitation spectra of porous Si (a) before and (b) after the 1-min photochemical etching. The luminescence spectrum is very sensitive to the fabrication conditions.

Fig. 3.4. The experimental results for size dependence of the PL peak energy in oxidized Si nanocrystallites at room temperature are reproduced from Ref. [20] (●), Ref. [48] (○), and Ref. [71] (▲). Theoretical curves for the band-gap energy are represented by solid (Ref. [63]), broken (Ref. [66]), and dotted (Ref. [69]) lines. The size dependence of the luminescence peak energy is very small compared to that of the theoretically calculated band-gap energy.



Typical optical absorption and photoluminescence spectra of porous Si films at room temperature: 2 nm, (b) $L \sim 3.5$ nm, and (c) $L \sim 9$ nm. The size L is determined from Raman spectroscopy and TEM. The ntial absorption tail is observed. No significant size dependence of the luminescence spectrum is observed (from itsu et al. [41]).

Band-gap energy as a function of the diameter of crystalline Si spheres. The solid and open circles correspond to nd-gap energy of porous Si and oxidized Si nanocrystallites, respectively. The solid line represents a theoretical tion for the size dependence of the band-gap energy of crystalline Si spheres, based on an effective-mass mation (Ref. [66]). In small nanocrystallites, the band-gap energy is consistent with the calculation in Ref. [62].

Published (good) work in nanometer-size Si particles.

Wang & Zunger: empirical pseudopotentials
J. Phys. Chem. 98, 2158 (1994)
(really semiempirical)
geometry modelled to bulk,
different surfaces
(good sense at corners??)
LDA (optical transitions?)
emission too high

Allan et al :
Phys. Rev. Lett. 76, 2961 (1996)
"big" tight binding
(empirical)
geometry modelled
"small" first principles ($N \leq 10$)
geometry "guessed"
defects needed

Kumar et al :
Jpn. J. Appl. Phys. 33, 909 (1994)
"small-medium"
semiempirical LCAO
(molecular parametrization)
emission too high

Very difficult problem!

eigenvalue problem $\langle \psi_i | H | \psi_i \rangle$ at each geometry: dimensions?

orthogonalization step scales as N^3

number of atoms

First-principles calculations (LDA or HF)

bulk (N=2) ☺

defects, supercells (N~50) } 😐 very costly

molecules, clusters (N~100) }

{ geometry optimization for $N \leq 10$ atoms,
"educated guesses" for sample configurations

Empirical calculations (TB)

bulk, cluster, ... $N \sim 10^4$ ☺

😐 { no real account for charge rearrangements
no real account of geometries

Existing semiempirical techniques

😐 designed for molecules,
extremely poor description for bulk

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This work: Semiempirical LCAO techniques

Hartree-Fock-Roothaan: $\hat{F}\psi_i = E\hat{S}\psi_i$

LCAO for ψ_i's $\quad \psi_i(\vec{r}) = \sum_{I,\mu} C^i_{I\mu}\,\phi_\mu(\vec{r}-\vec{R}_I)$

ZDO for $\hat{S}$ $\quad \phi_{\mu I}\phi_{\nu J}\,d\tau = \delta_{\mu\nu}\delta_{IJ}$

Very successful semiempirical implementations for molecules (chemistry) $\quad I,J = 1 \cdots N$ finite!

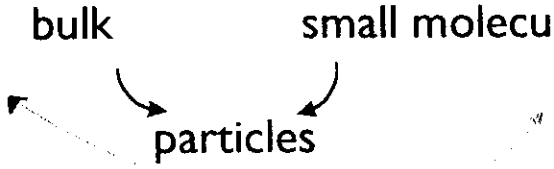
Modified Neglect of Diatomic Overlap
- geometries, vibrational frequencies
- several parametrizations MNDO/AM1, PM3, ...

Intermediate Neglect of Differential Overlap
- optical properties
- several parametrizations INDO/1, INDO/2, ZINDO

Here: Reparametrize!

- HFR method for crystals (bulk)
  - Bloch sums
  - Bloch hamiltonian
- Pseudo-atom method for nanocrystals
  - (pseudo-Si to terminate clusters)
- New parametrizations
  - MNDO/Crystal
  - INDO/Crystal

Si, α-Quartz, SiH_4, Si_2H_6, Si_2OH_6, ...



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AM1/Crystal: Fit for the Silicon Crystal

Bulk Modulus (10^{12}dy/cm^2), equilibrium lattice parameter (Å)

	Cell	BZ Point	Neighbours	Lattice Parameter	Bulk Modulus
☺	8	4	3	5.453	1.125
	64	1	5	5.475	1.123
	64	4	5	5.454	1.120
☹					
	Experimental			5.429	0.978

* Original Parametrization

Phonon Frequencies (cm^{-1}) for Si Crystal

BZ Point	AM1/Crystal	Experimental
LTO(Γ)	522	517
LAO (X)	427	410
TO (X)	481	463
TA(X)	175	150
LO(L)	430	417
LA(L)	392	378
TO(L)	492	487
TA(L)	142	114

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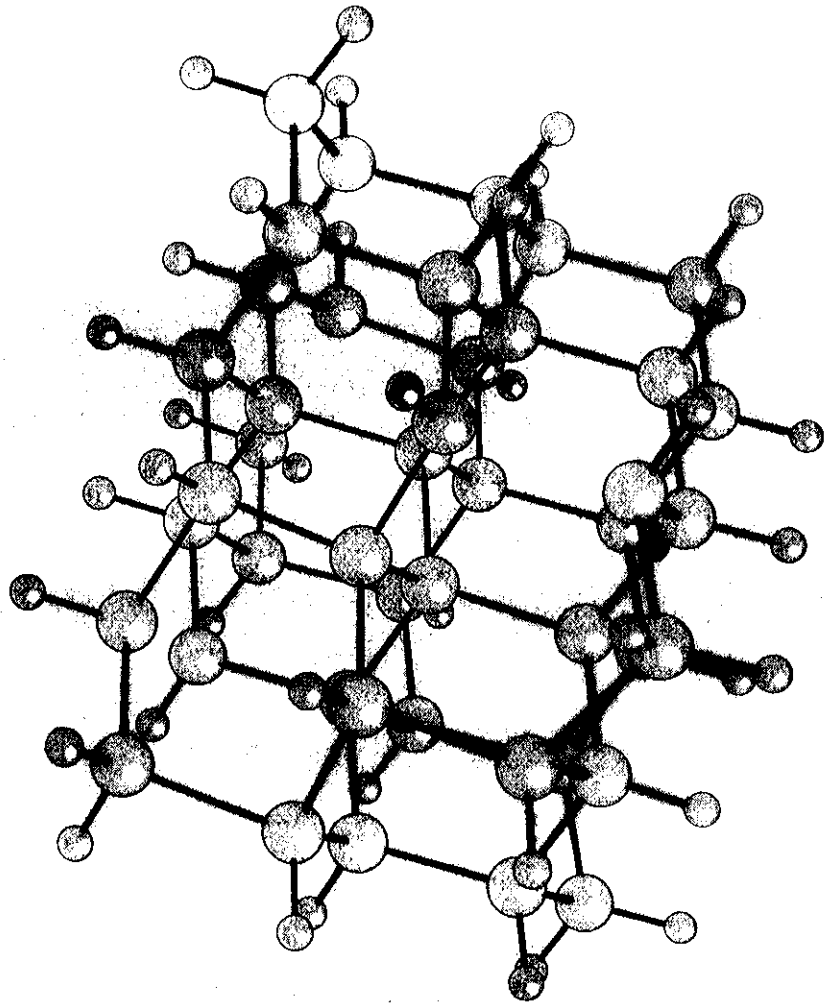
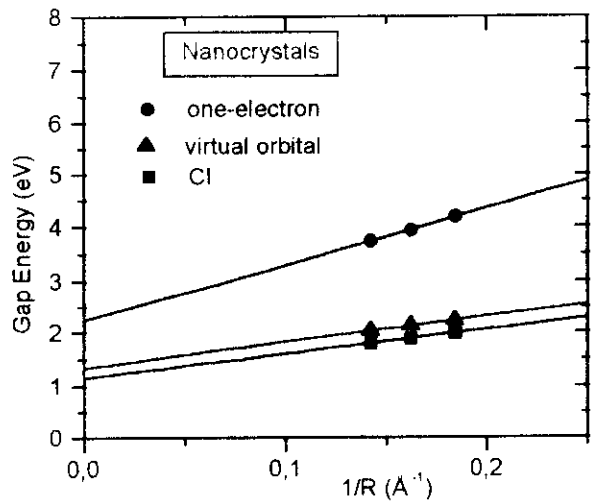


Calculation of energy-gap for periodic systems

problems with HF, impossible CI

INDO/Crystal HF for periodic bulk (Bloch)
valence band, indirect "gap".

INDO/Crystal/CI for nanocrystals
finite nanocrystal ⟶ "infinite" limit



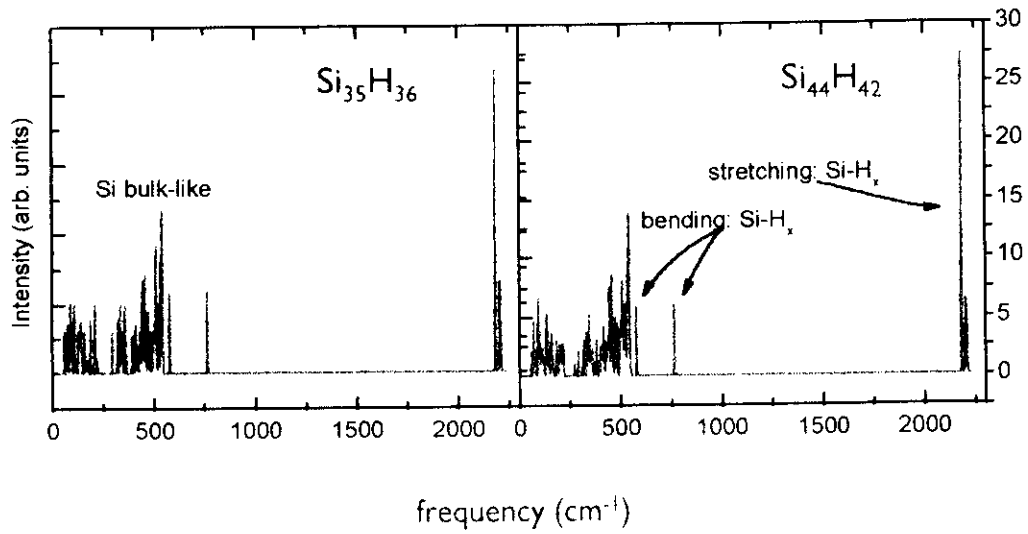
Correlation: HF $\Psi_G = AP[\{\psi_i\}]$, i = occupied
excited states? transition energies?
eigenvalues $\epsilon_j - \epsilon_i \neq E^{exc}_{+j-i} - E^G$!
1st correction: energy of $\psi_\alpha = AP[\{\psi_m\} - \psi_i + \psi_j]$
↓ for finite systems, correction good "basis" for
2nd correction: Configuration Interaction

$$\Psi_\Gamma = \sum_\alpha C^\Gamma_\alpha \psi_\alpha$$

Results: Si-H particles in different symmetries

T_d (atom-centered) up to $Si_{71}H_{60}$
D_{3d} (bond-centered) up to $Si_{44}H_{42}$

MNDO/Crystal: relaxed optimal geometry
all atoms in particle



Small particles already reproduce Bulk Phonon dispersion

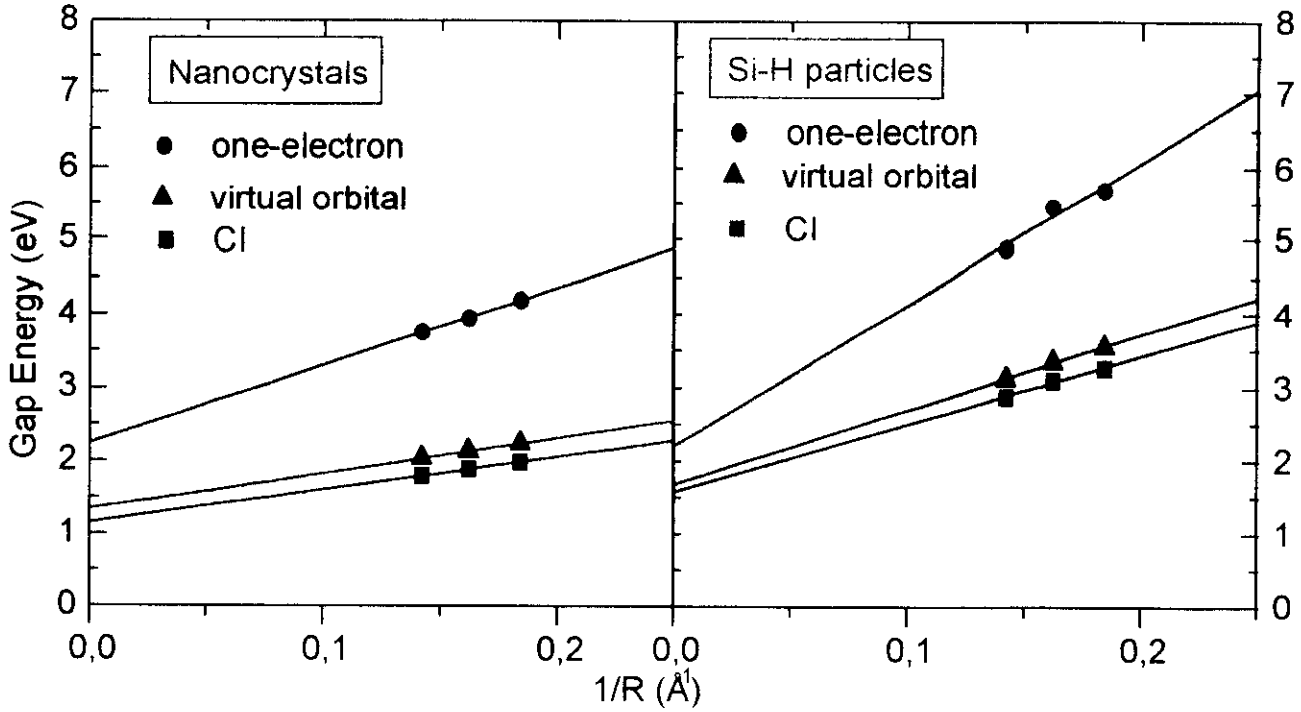
Split-off mode: Compression of Central Shell

Results: Si-H particles in different symmetries

T_d (atom-centered) up to $Si_{71}H_{60}$
D_{3d} (bond-centered) up to $Si_{44}H_{42}$

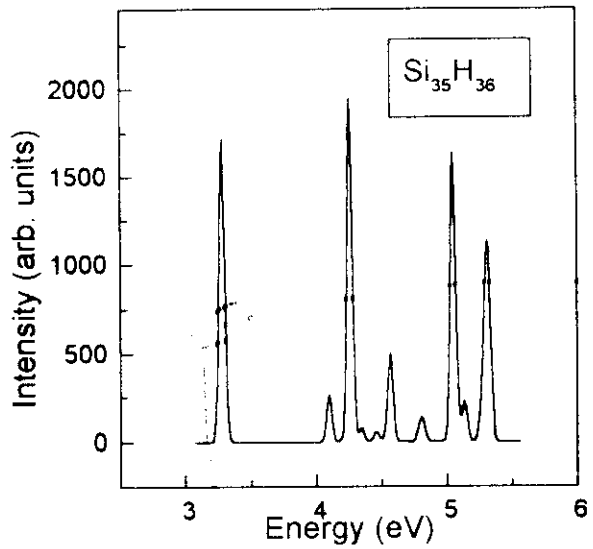
INDO/Crystal/CI: optical absorption

Result: Right trend for the absorption of Si-H particles
Correct energies



Relaxation!

Result: emission too high!

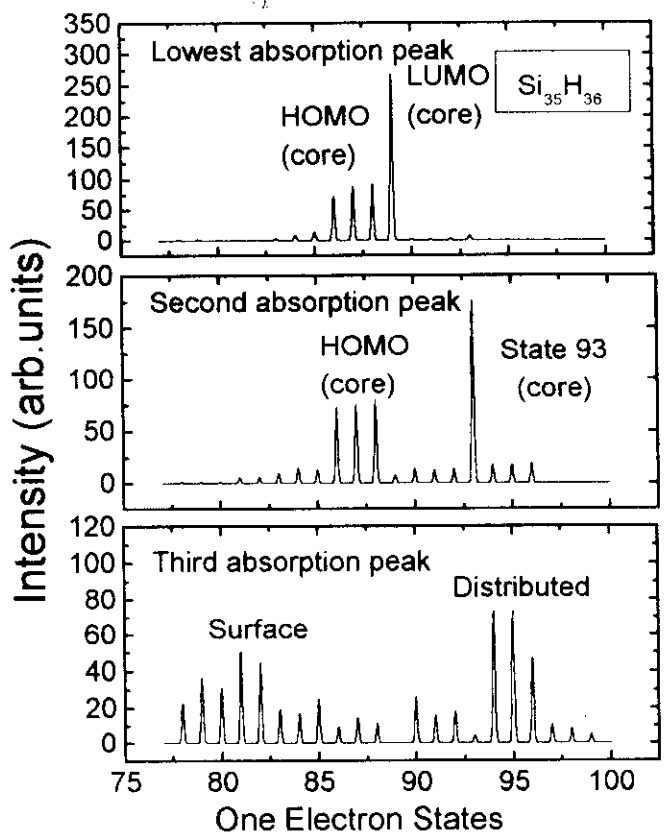


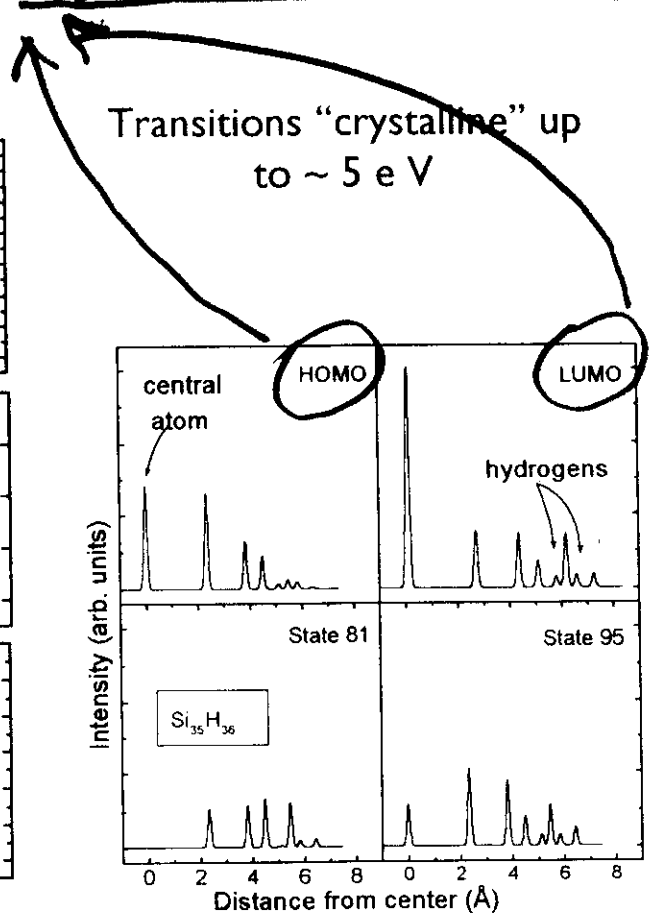
Results for $Si_{35}H_{36}$

Td-symmetric particle

1st absorption HOMO-LUMO
(very little CI)

Originates in the crystalline Si core





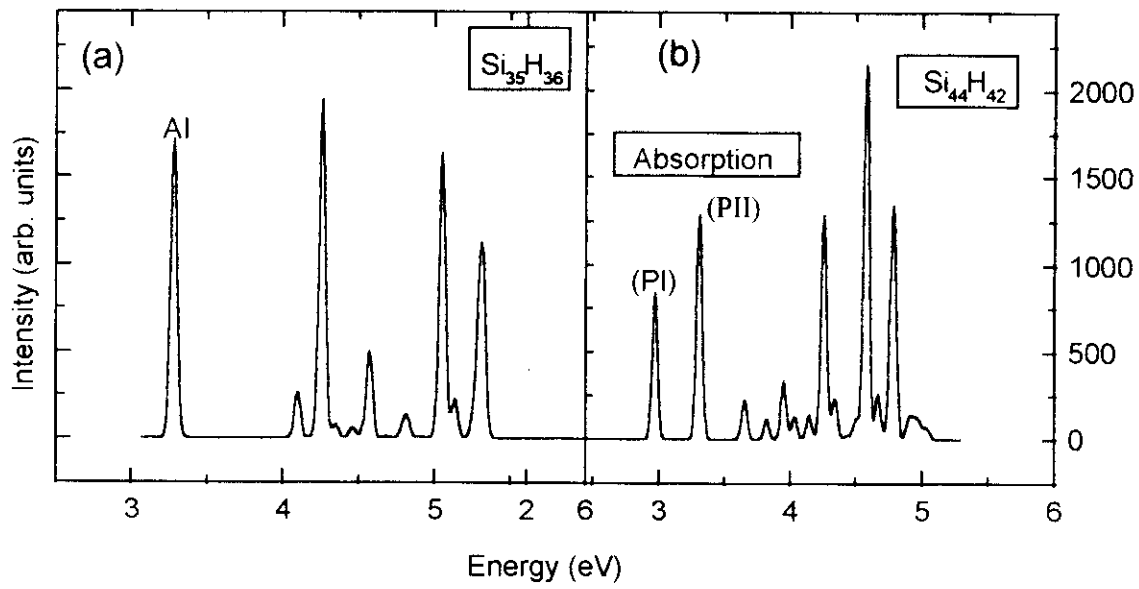
Effect of symmetry?

no, results very similar for D_{3d} - symmetric particles

symmetry-splitting $t_2 \longrightarrow a_1 + e$ (HOMO)

T_d $\quad {}^1A_1 \longrightarrow {}^1T_2$

D_{3d} $\quad \begin{cases} {}^1A_1 \longrightarrow {}^1A_1 \\ {}^1A_1 \longrightarrow {}^1E \end{cases}$



Now What?

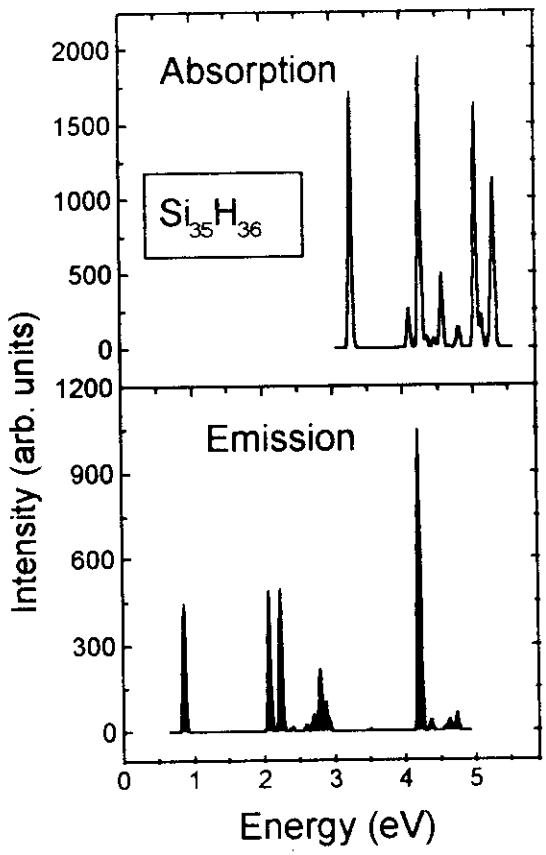
Particle is sufficiently small

⟶ relaxation in excited state?
(stokes, Franck-Condon, ...)

first absorption almost pure <u>one-electron excitation</u> HOMO-LUMO

MNDO/Crystal $Si_{35}H_{36}$, $Si_{44}H_{42}$

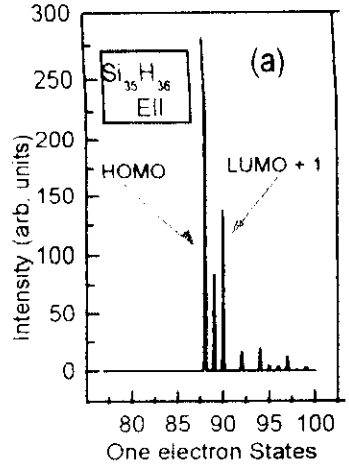
allow relaxation again



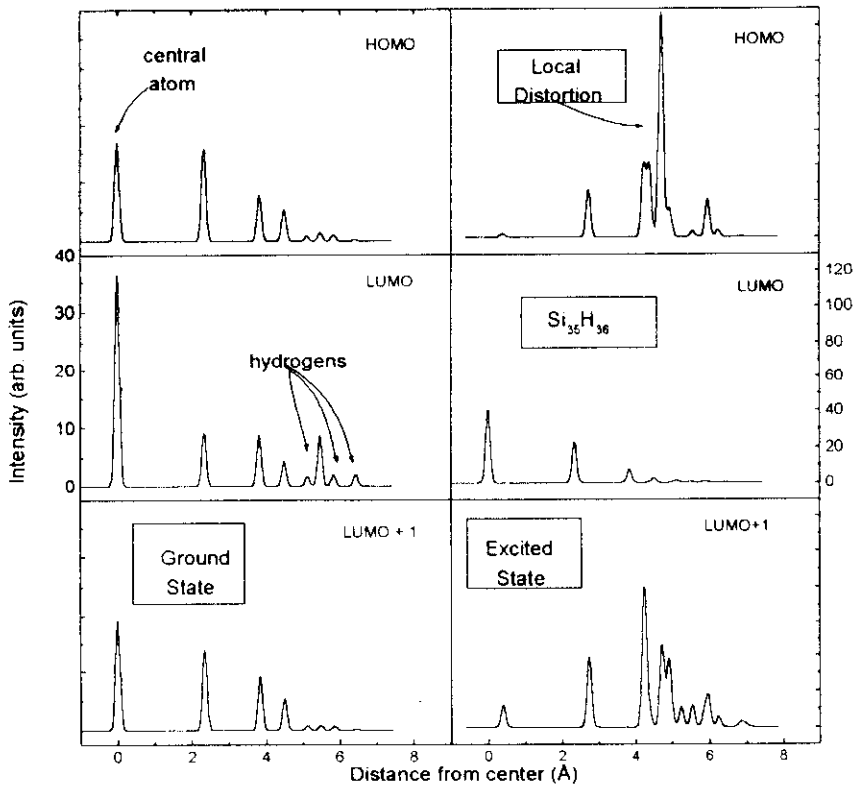
INDO/Crystal/CI for ground state configuration
absorption spectra

INDO/Crystal/CI for <u>excited state configuration</u>
⟹ <u>emission spectra</u>!

What is happening?



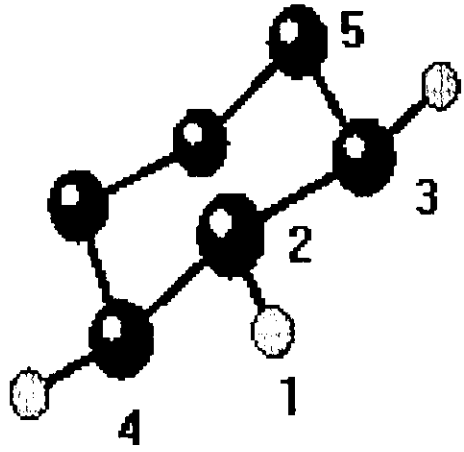
Transition no longer pure one-electron



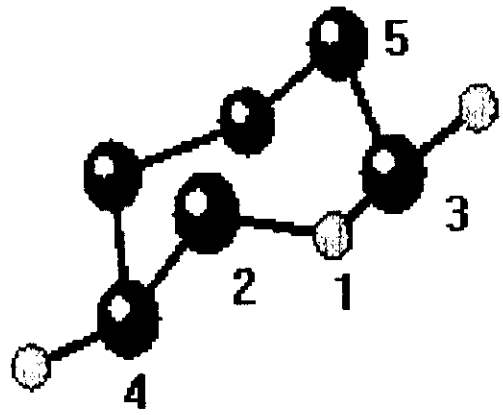
HOMO & LUMO+1 very localized

Photogenerated "Bridge" defect

Bond	Ground State		Excited State	
	Index	Distance	Index	Distance
Si_5 - Si_3	0.914	2.351	0.854	2.365
Si_3 - Si_2	0.919	2.367	0.398	2.634
Si_4 - Si_2	0.008	3.184	0.541	1.546
Si_2H_1	0.956	1.476	0.392	1.673



Ground State



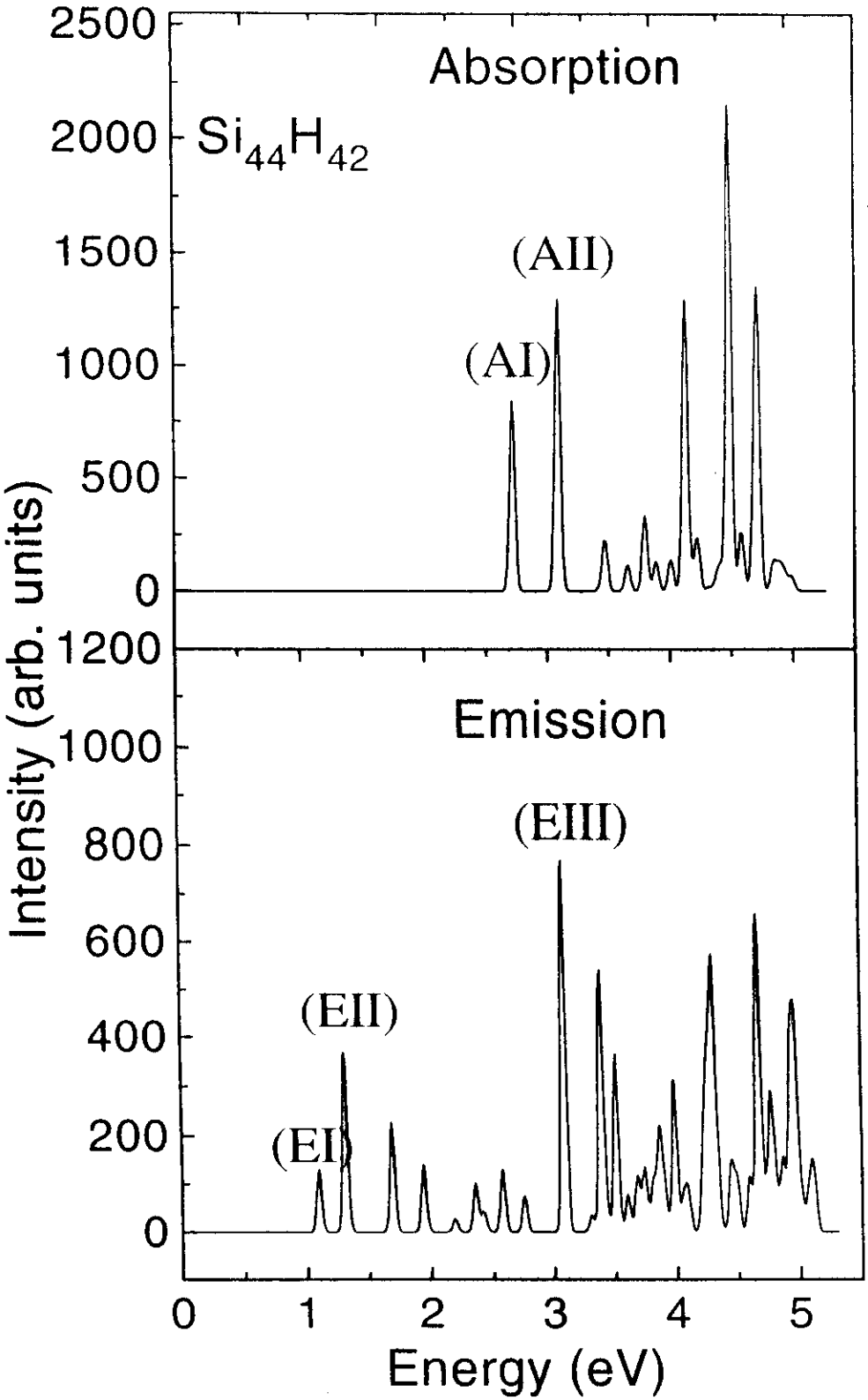
Excited State

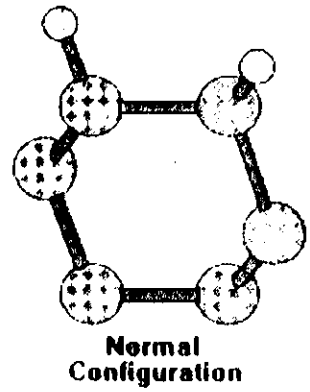
Si-Si bond not broken

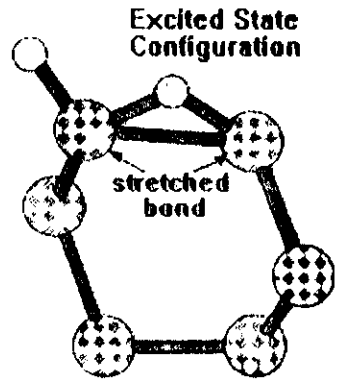
↯

Configuration not metstable, highly unstable

Effect of Symmetry?

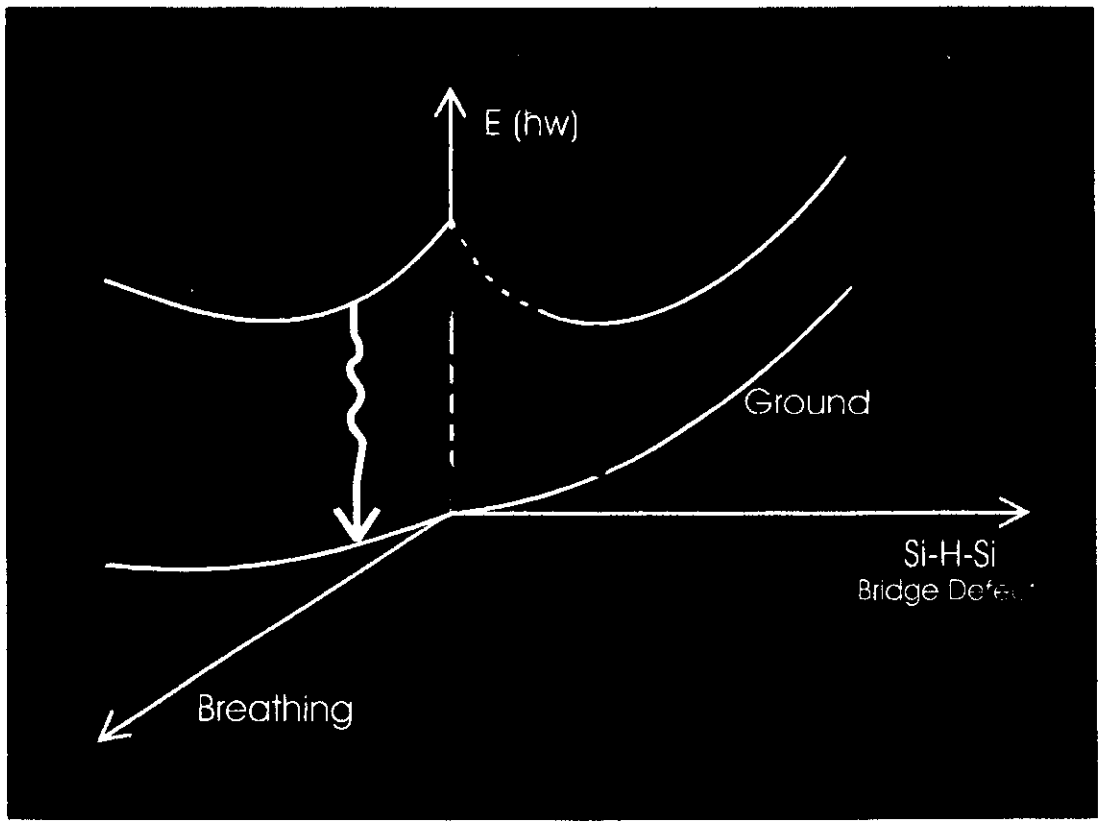






Model: Configuration Coordinate

Absorption (core) ⟶ Spontaneous defect
"exciton" trapping?



Red Luminescence ⟶ back to normal

no bleaching, no damage

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Conclusions I

Si-H particles can explain po-Si

Absorption
- Size-dependent
- Crystalline ⟹ confined
- Relaxed ⟹ blue-shifted
- No hydrogens!

Emission
- Blue-Green: Crystalline, fast
- Red-Orange: Pinned by Si-H-Si defect
  Hydrogens essential (!)
  "Softness" essential

Photogenerated Defects: everywhere?
(EL2 ....)
certainly in rough, soft environments

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Some References

(only those that are not quoted in the notes themselves)

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