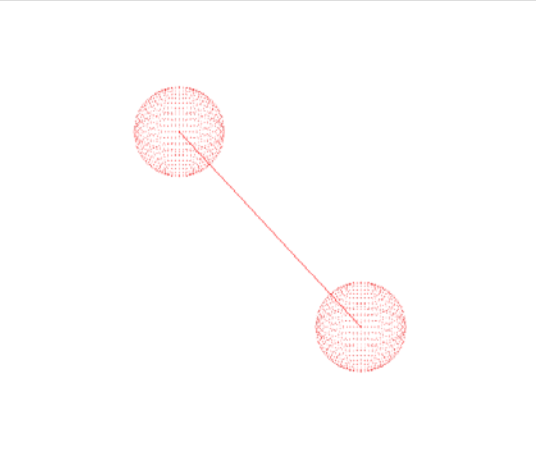
Interaction of electromagnetic fields with molecular rotors. Coherent dynamics and transfer of energy at quantum systems.

Motivation and target of nanotechnology

To construct molecular engines below 100 nm with specific functionality.



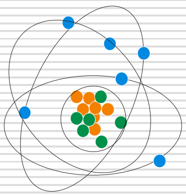
How;

1)By decoding physical laws in the mesoscopic region (<100nm).
2)Controlling the parameters.
3)Implementing the technology.

I) Top down → lithography (40 nm)

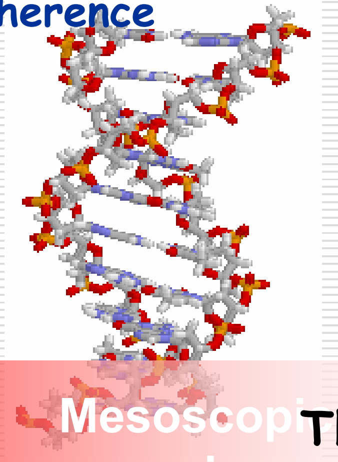
II) Bottom-up → Imitating and copying nature (1-10 nm)

Decoding the physical laws

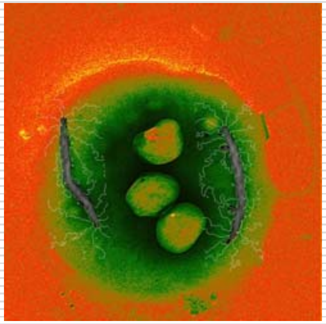


1)Polar–entropic competition.
2) Flow of energy at interphases
3) Long range fields
4) Asymmetries
5) Quantum effects-coherence

- polar bonding (hydrogen)
- Entropy (hydrophobicity)



Self assembly
Molecular engines-motion
Molecular rotors-transfering and storing energy



Quantum mechanics

Mesoscopic region

Thermodynamics, hydrodynamics

1nm 10nm 100 nm

Outline

- A Working experimental example
- Control over crystallization and shapes at the nanoscale

Questions to be addressed

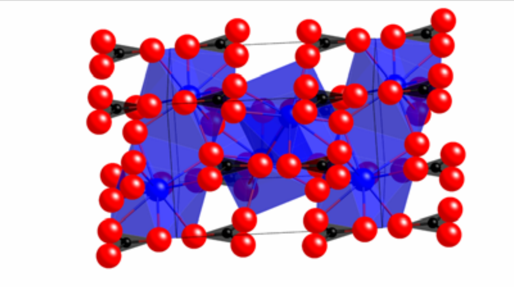
- (1) Transfer of energy
- (2) Storage of energy

Through coherent interactions→ EMF-matter

- The symmetric-antisymmetric coherent state at the nanoscale
- Industrial applications

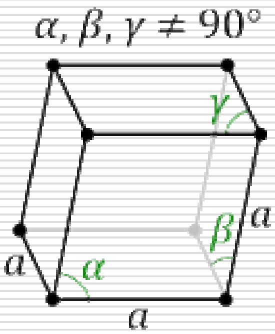
Facing experimental challenges

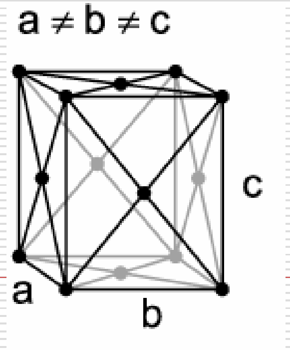
Would be possible to control nano-crystallization symmetry?

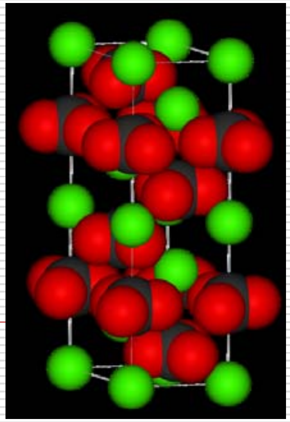


Crystal symmetry of $CaCO_3$

Calcite	Orthorombic
Aragonite	Triclinic
Vaterite	Amorphous

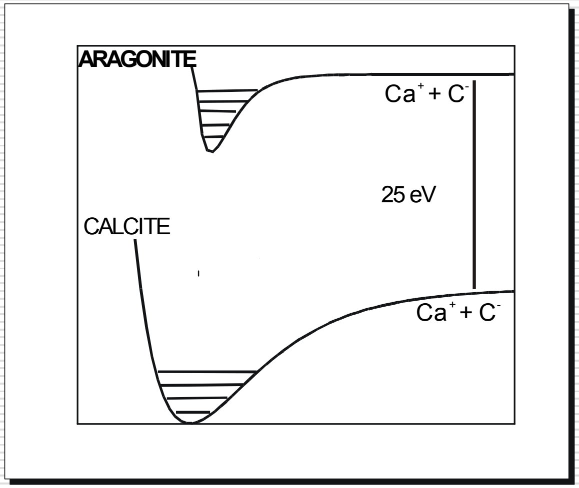






Free energy of formation

Ground electronic states of calcite and aragonite separated by 25 eV- (ab-initio).

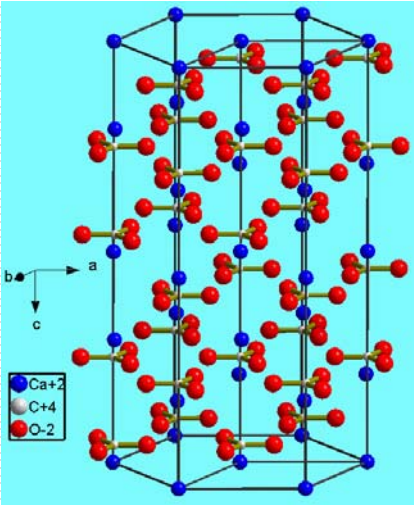


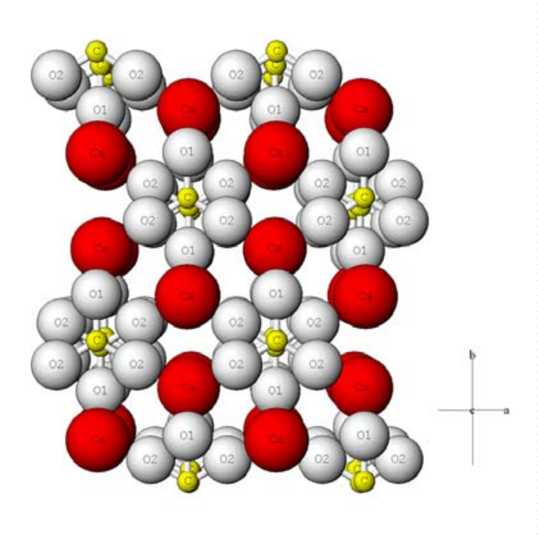
$$F_A = F_c + \Delta F(25eV)$$

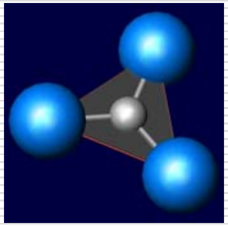
$$F(T,P) = F_A(T,P)$$

A. C. Cefalas, et al, Cryst. Eng. 5, 243 (2002)

Required energy





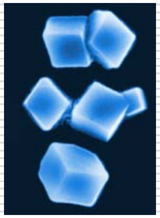


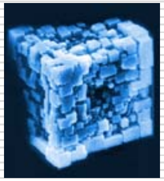
$$h\nu = 49.5nm,\ T = 2X10^{5}\ K$$

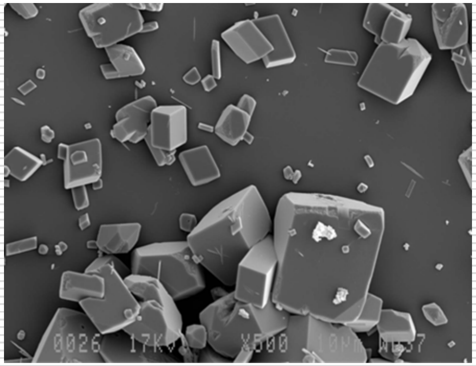
per molecule

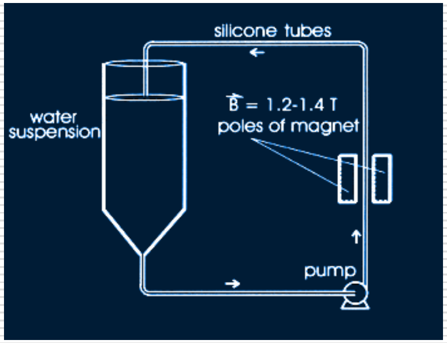
$$\Delta F = 10^{12}\ \mathrm{J/m^3}$$

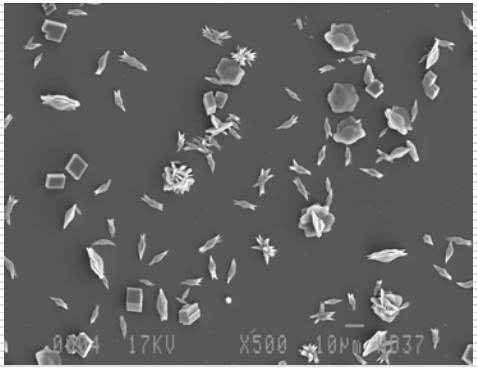
A simple experiment

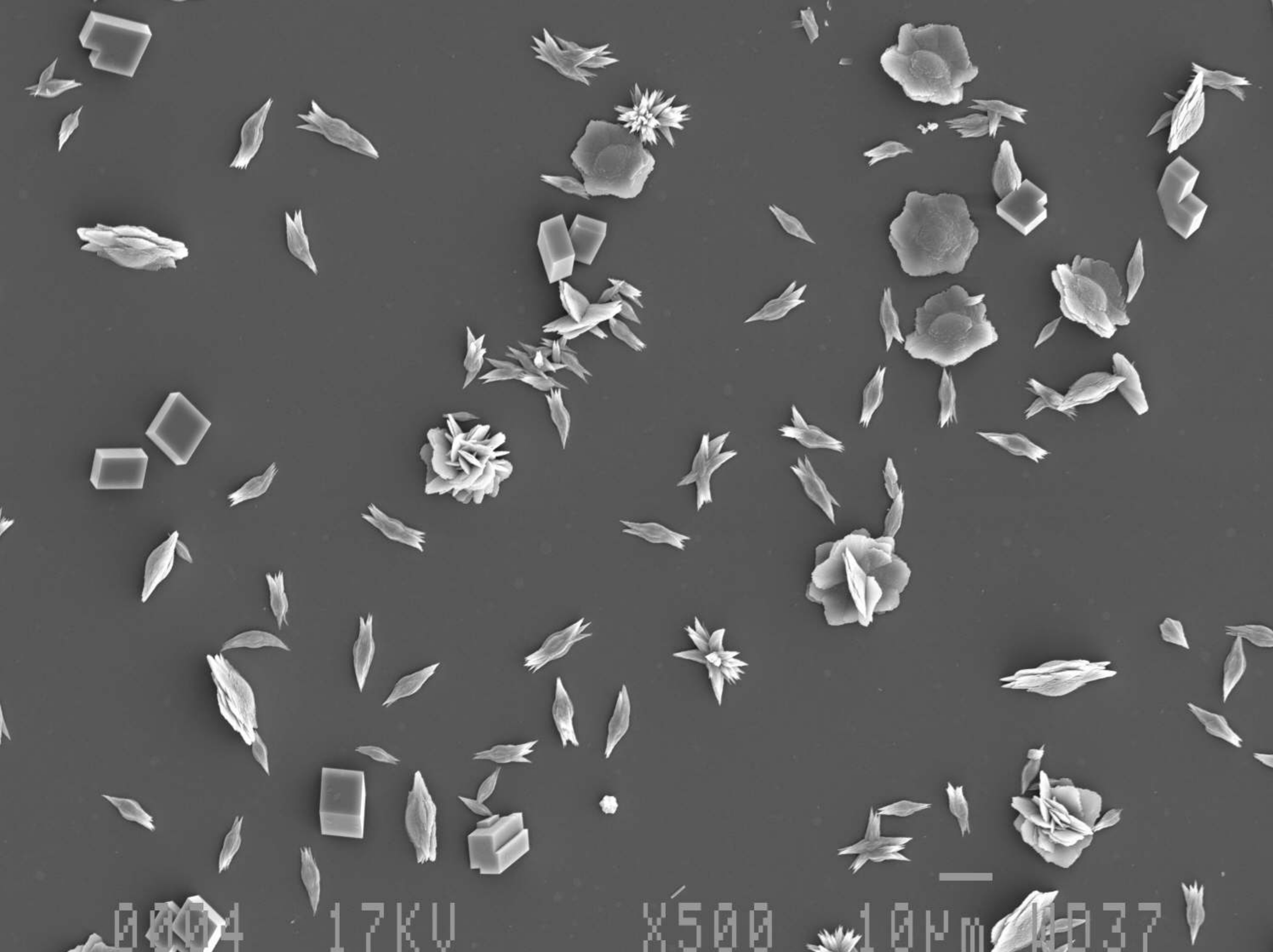











0004 17KV X500 10μm WD37

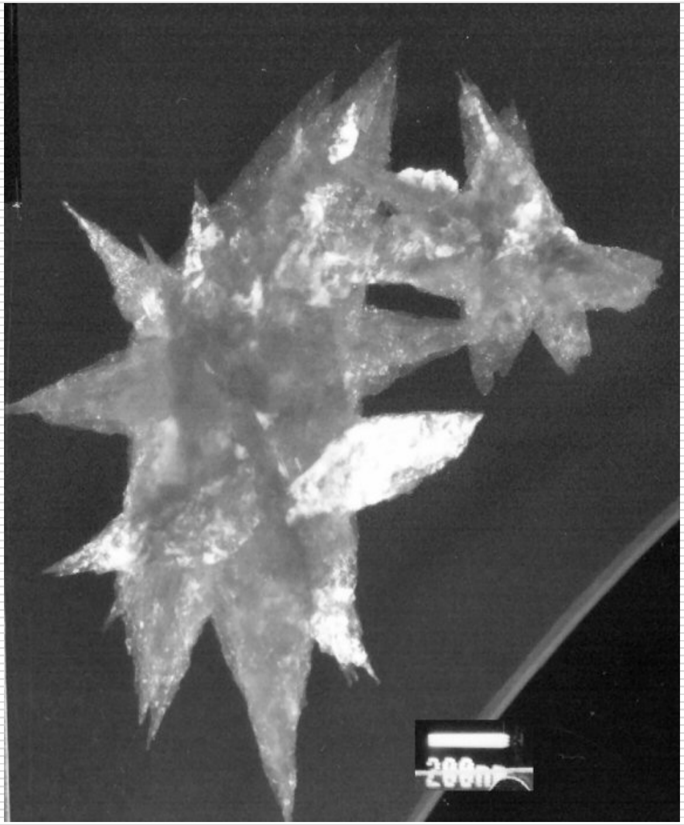
TEM images of structures

A

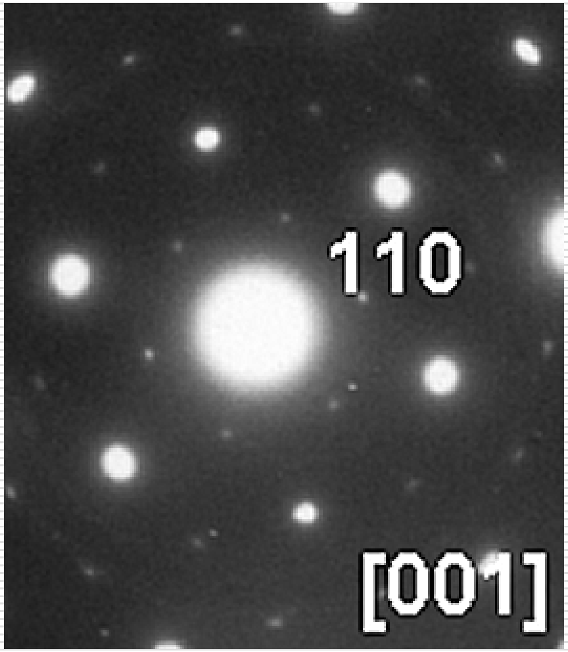
B

(A) TEM image. (B) diffraction pattern (SAED). →Calcite

A

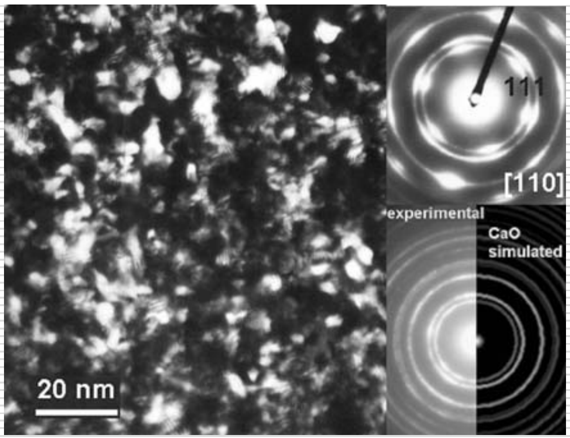


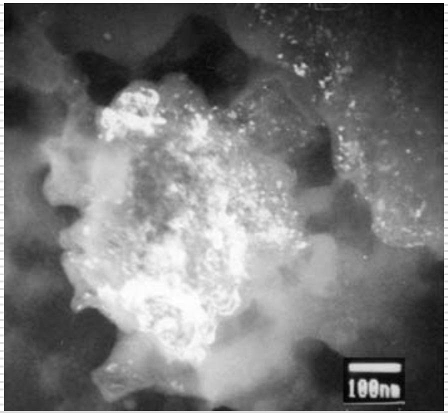
B



(A) TEM image. (B) diffraction pattern (SAED). Aragonite

TEM - Vaterite

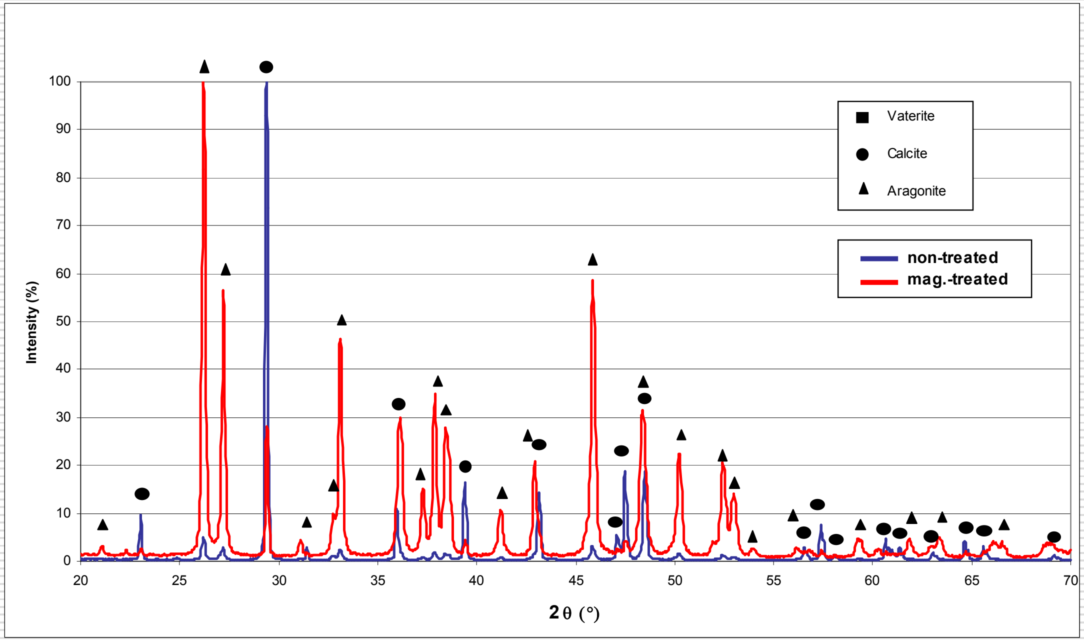




- Decomposition of vaterite phase under the electron beam
- Formation of 5 – 10 nm sized crystals of CaO.

- SAED pattern of decomposed vaterite crystals where spots (arcs) indicate texture of CaO in [110] zone axis. Circles correspond to randomly oriented nanocrystals of CaO.
- The comparison of experimental and simulated SAED patterns for cubic (Fm3-m) CaO.

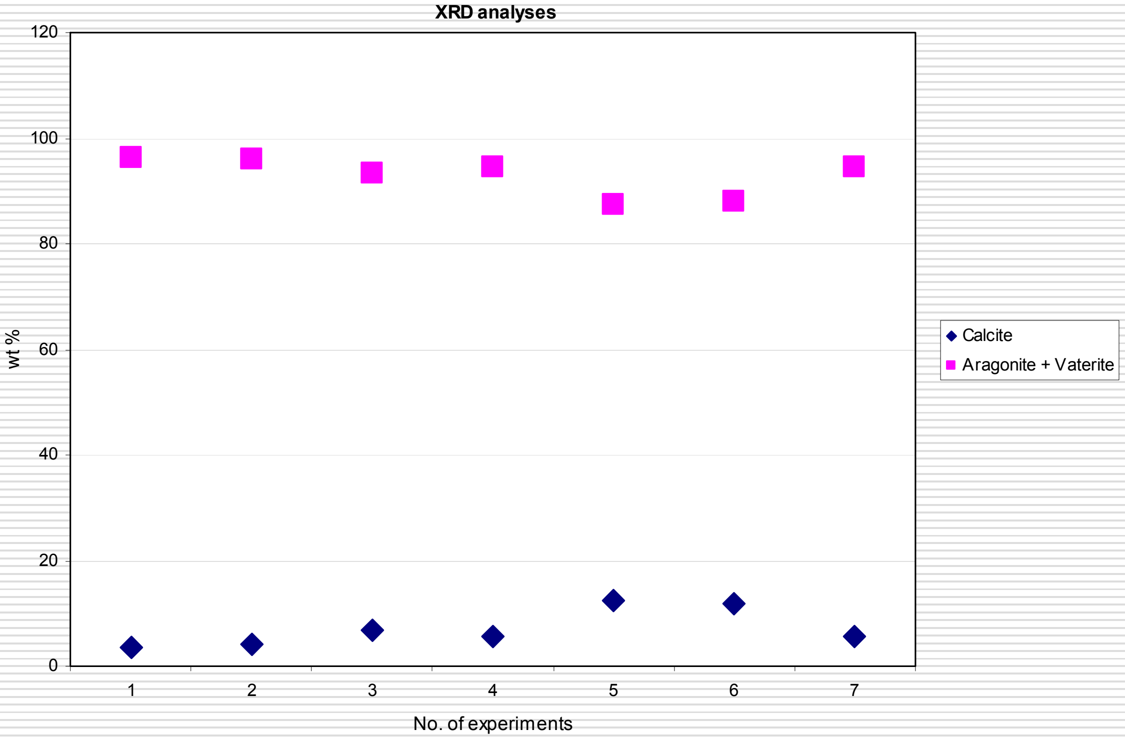
X - Ray Analysis



Quantitative X-ray analyses of crystals

Experiments	Magnetic field	Calcite (%)	Aragon. (%)	Vaterite (%)
1-7	0	90.2	9.6	0.2
1-7	400 mT	80.0	10.4	9.6
1-7	1250 mT	12.5	87.0	0.5

Reproducibility of results at 1.2T

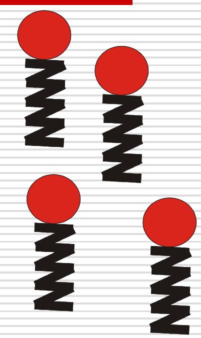


Questions to be answered

- From where the system takes its energy to change its thermodynamic state to form aragonite in solutions.
- How the energy is stored and then is amplified?
- Classical models have failed till now!
- Quantum theory

Quantum picture

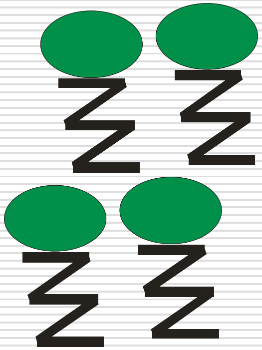
$$\hat{H}_F = \sum_k h\omega_\kappa \hat{\alpha}^+_\kappa \hat{\alpha}_\kappa$$



$$\hat{H}_A = \hbar \sum_i \hat{\sigma}^+_i \sigma_i \omega_{iR}$$

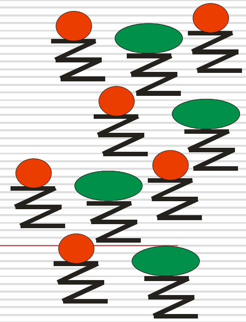
$$\hat{\sigma}^+ = \hat{J}^+ = \hat{J}_x + i\hat{J}_y$$

$$\hat{\sigma} = \hat{J}^+ = \hat{J}_x - i\hat{J}_y$$



$$H_{\text{int}} = (\frac{i\,\mathrm{e}\mu_0}{2\mathrm{m}}) \sum_{k\lambda} (\frac{\hbar c^2}{2\mu_0 \tau \omega_\kappa})^{1/2} [(\hat{i} - \hat{j})\hat{\sigma}^{\wedge +} (\hat{a}_{\kappa\lambda} \exp(i(-\omega_\kappa t) +$$

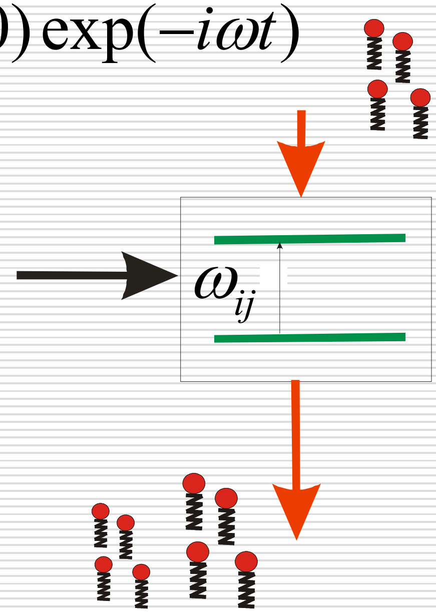
$$(\hat{i} + i\hat{j})\hat{\sigma}^{\wedge} (\hat{a}^+_{\kappa\lambda} \exp(i(\omega_\kappa t)) + 2(\hat{i} - \hat{j})\hat{\sigma}_{\omega R}{}^+ (\hat{a}_{\kappa\lambda} \exp(i(-\omega_\kappa t) + 2(\hat{i} + i\hat{j})\hat{\sigma}_{\omega R} (\hat{a}^+_{\kappa\lambda} \exp(i(\omega_\kappa t))$$



Maser model-amplification

$$a(0)\exp(-i\omega t)$$

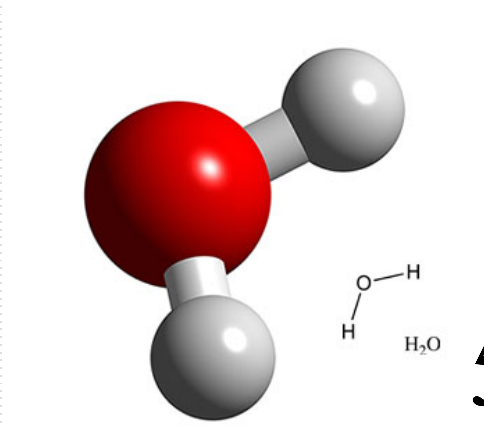
$$\Omega_B = \frac{G_R \beta B}{\hbar \mu}$$

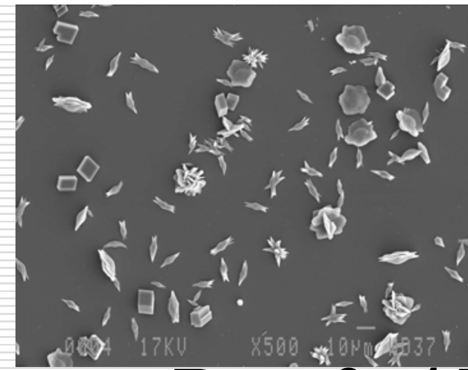


$$\langle \mathrm{n} \rangle = \langle a(t)^+ \left| \alpha(t) \right\rangle \approx \langle a(0)^+ \left| \alpha(0) \right\rangle ((\omega^2 + \frac{\gamma^2}{4}(\tanh \frac{\hbar B}{2g\mu k T_\sigma} t)^2)^{\frac{1}{2}}$$

$$\omega = \omega_{ij} = \Omega_B \Rightarrow \gamma, n \to \infty$$

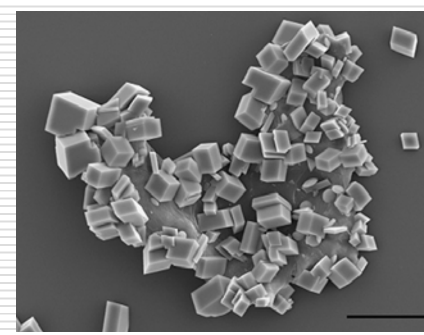
Amplification in water molecular rotors





$$5_{-1} \rightarrow 6_{-5} \rightarrow \omega_{ij} \Rightarrow B = 0.4T$$

$$\omega_{ij} = 2.2x10^{17}\, s^{-1}$$

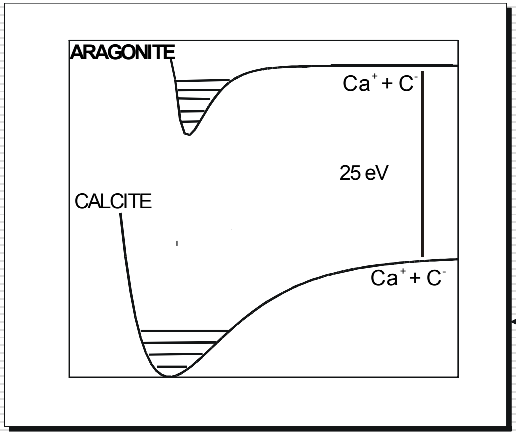


In agreement with experimental results

A.C. Cefalas etal, Appl.Surf. Scienc.25,6715 (2008)

Still questions remain –

High free energy difference → energy storage



$$F_A = F_c + \Delta F\,(25eV)$$

$$F(T,P) = F_A(T,P)$$

$$\Delta F = 10^{12}\,Jm^{-3} \Rightarrow B = 480T$$

A. C. Cefalas, et al, Cryst. Eng. 5, 243 (2002)

Two atom single mode interaction

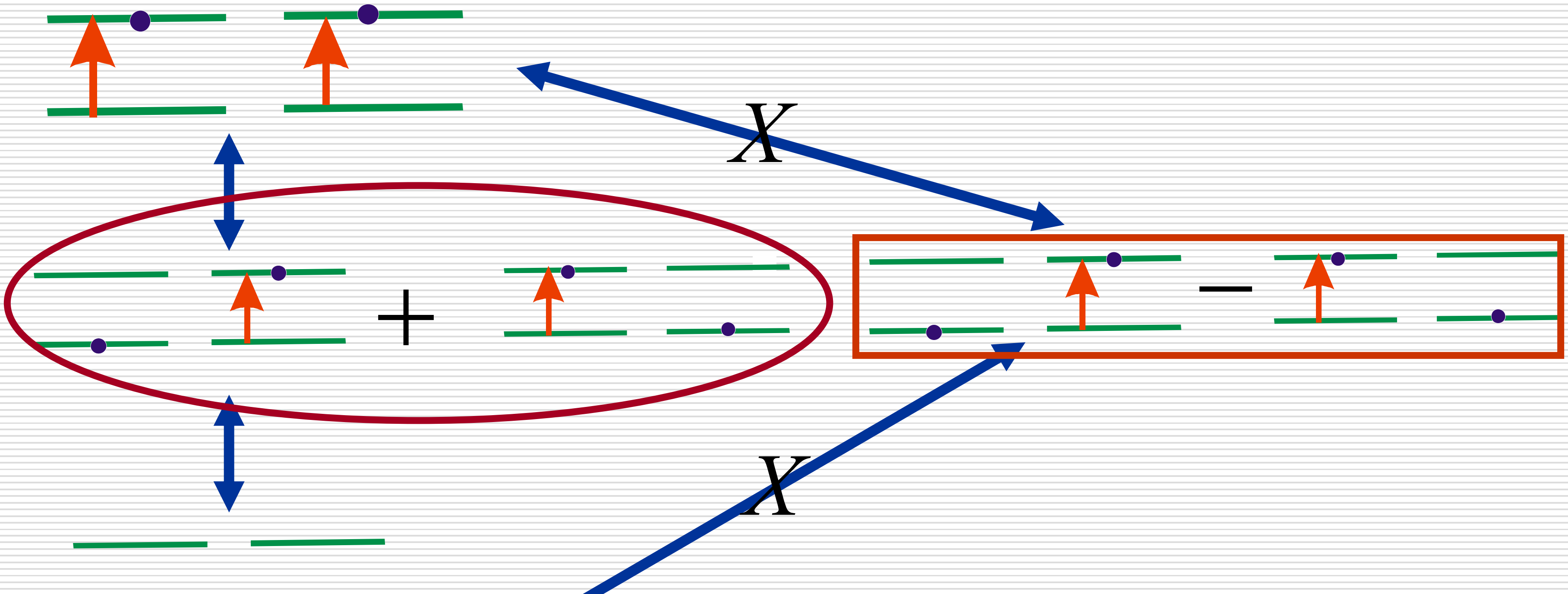
$$|\psi(t)\rangle = U(t,0)|\psi(0)\rangle$$

$$|\psi(0)\rangle = |b_1 b_2\rangle |2\lambda\rangle$$

$$U(t,0) = 1 - \frac{i}{\hbar}\int_0^t H_{\text{int}}(s)ds + ..$$

$$H_{\text{int}} = g_\lambda[(\sigma_1 + \sigma_2)\exp(\omega_{ij} - \omega_\lambda)t]a_\lambda^+ + adj.$$

Mode trapping in coherent antisymmetric states



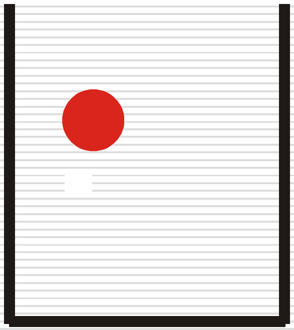
$$|\psi(t)\rangle = C_0|b_1b_2\rangle|2\lambda\rangle + \sqrt{2}C_1\{[|a_1b_2\rangle + |a_2b_1\rangle] + [|a_1b_2\rangle - |a_2b_1\rangle]\}|1\lambda\rangle\sqrt{2}C_2|a_1a_2\rangle|0\lambda\rangle$$

A. C. Cefalas, et al Journ. Comput Theor.NanotechnologyV7, 1800 (2010)

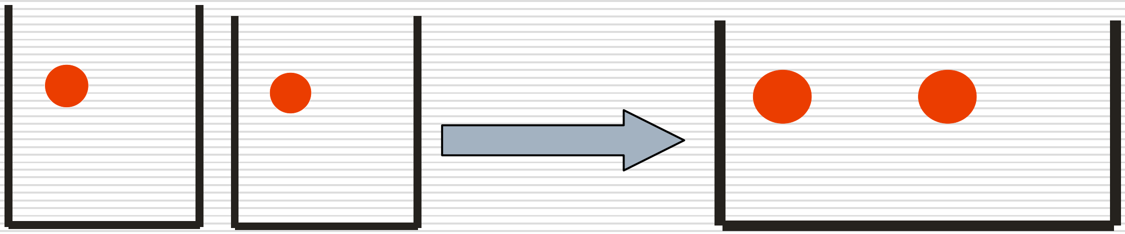
The coherence

Particles in a small box → Quantum physics
Particles in a large box → Classical physics

$$E(J)=\frac{\pi^2\hbar^2}{2mL^2}(n^2+m^2+l^2)\Rightarrow$$



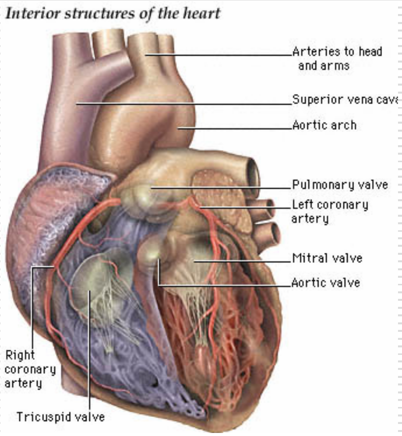
particles in a large box→quantum



Applications

Implications

→**Calcite: Strong Binding with surfaces**
→**Aragonite: Weak binding with surfaces**



Scale formation (water pipes)

Water pipes → calcium carbonate scale

prevention: chemicals

environmental pollution

Chemical treatment has a long-term environmental accumulative effect;

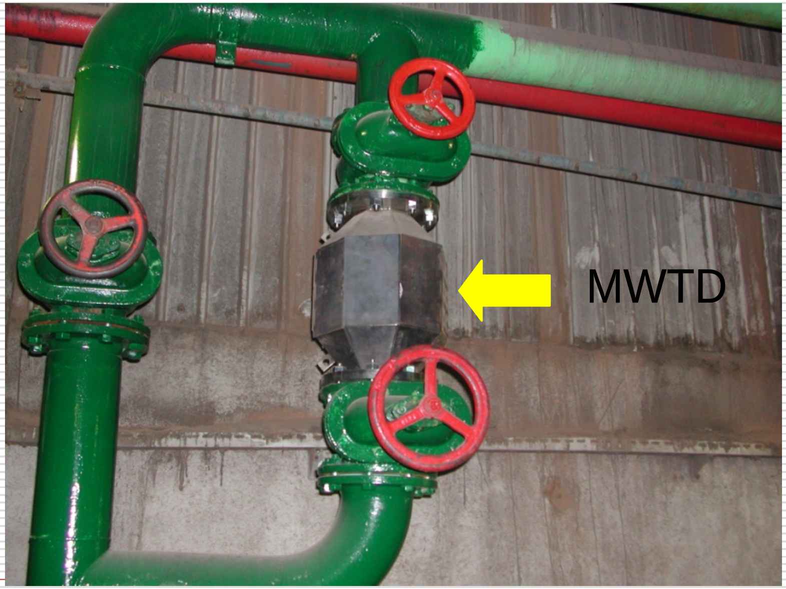
It is detrimental for sensitive ecosystems, the most serious been algae eutrification.

Economical impact

- In UK alone, the formation of scales in industrial processing plants where water is heated or cooled is estimated to cost £1 billion per year.
- Industrial costs due to scaling, represent an annual turn over globally more than 100 billion $/year.

Termoelektrarna-Toplarna Ljubljana

Clean energy for the environment



conclusions

- A quantum coherence can interpret energy flow and storage at the nanoscale level.
- By coupling EMF to molecular rotors, a collective antisymmetric quantum state (Coherence) can store the energy of the EMF field.
- Nanocrystalization **probes** the phenomenon at the nanoscale.
- The quantum coherent antisymmetric state interprets the ¨memory effects¨ observed in liquids by many investigators.
- Control of nanocrystalization can have major industrial applications.

- National Hellenic Research Foundation, Athens Greece

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