Sonochemical Reactions

Chemical changes/reactions induced by ultrasound

No direct interaction of ultrasound field with molecules (in contrast to photochemistry, …)

•Liquid phase reactions – chemical reactions driven by cavitation effects

• Solid state reactions – introduction of defects = speeding up diffusion

Sound

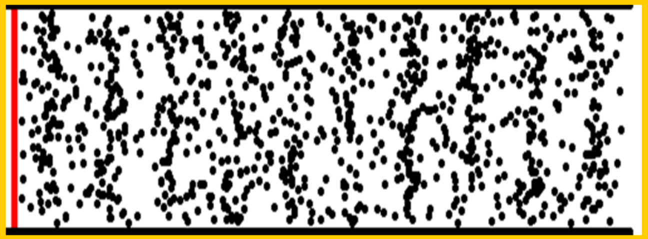
Sound = pressure waves = periodic compression/expansion cycles traveling through a medium possessing elastic properties (gas, liqud, solid)

Liquids and gases – longitudinal pressure waves – compression/rarefaction
Solids – longitudinal and transverse waves

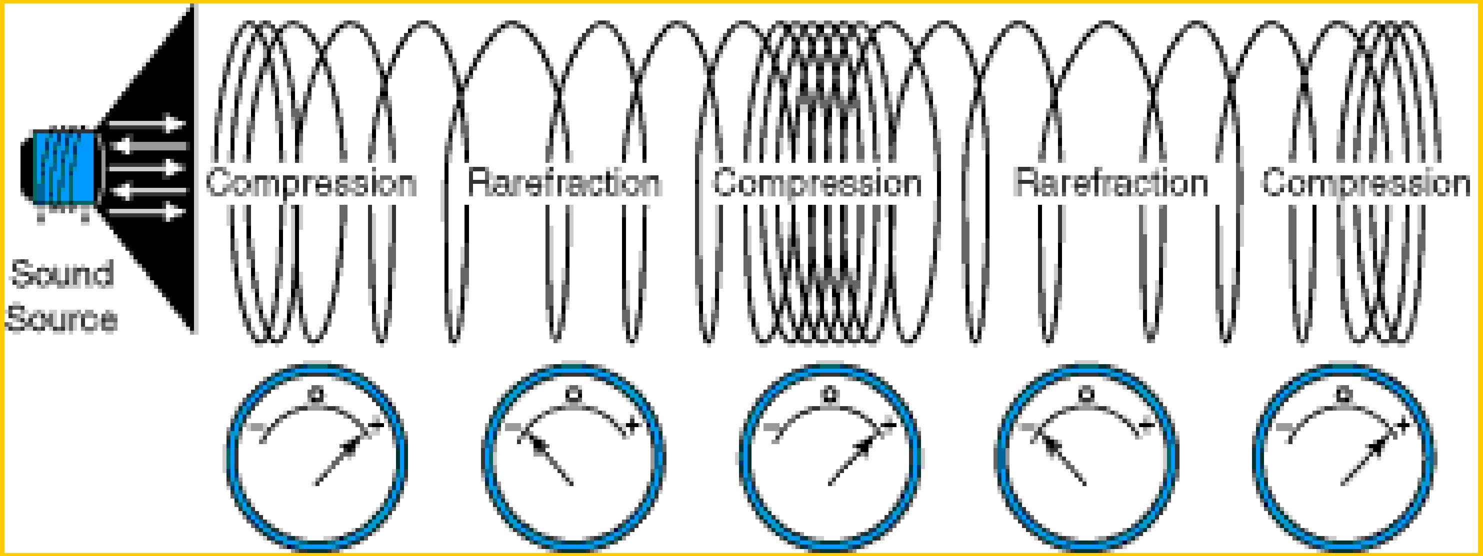
The energy is propagated as deformations (tensile/compressive stress) in the media

The molecules oscillate about their original positions and are not propagated

The propagation of a sound wave = the transfer of vibrations from one molecule to another



Longitudinal Pressure Waves



Sound

In a typical liquid, the speed of sound decreases as the temperature increases, at all temperatures.

The speed of sound in water is almost five times greater than that in air (340 m s^{-1})

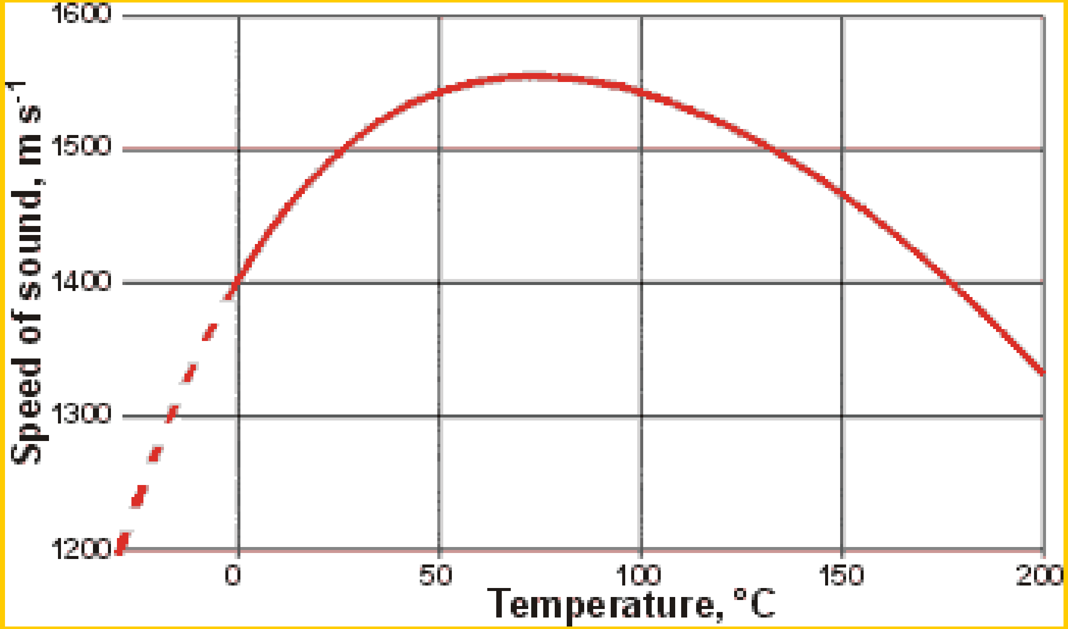
Substance	**Speed of sound, u [m s^{-1}]**
Air	**343**
Helium	**965**
Water	**1482**
Lead	**1960**
Steel	**5960**
Granite	**6000**

Speed of Sound

The speed of sound (*u*)

$$u^2 = 1/\kappa_S\rho = [\partial P/\partial\rho]_S \sim 1/(<(V)2>)$$

κ_S = **adiabatic compressibility**
ρ = **density**
P = pressure



Sound Intensity

Sound Intensity = Power / area = Watts/m^2

Source of Sound	*Intensity (W/m2)*	*Sound level (dB)*
Jet Airplane 30 m away	10^2	140
Air-raid Siren, nearby	1	120
Threshold of Pain	10^{-1}	120
Concert	~10^{-1}	115
Riveter	10^{-3}	100
Busy Traffic	10^{-5}	70
Normal Conversations	10^{-6}	60
Whisper	10^{-10}	20
Threshold of Hearing	10^{-12}	0

0 dB (10^{-12} W/m^2)
10 dB = 10 as intense
20 dB = 10^2 as intense
30 dB = 10^3 as intense
120 dB = 10^{12} as intense

Acoustic Pressure

$P_a = P_A \sin 2\pi f t$

P_a acoustic pressure

P_A pressure amplitude

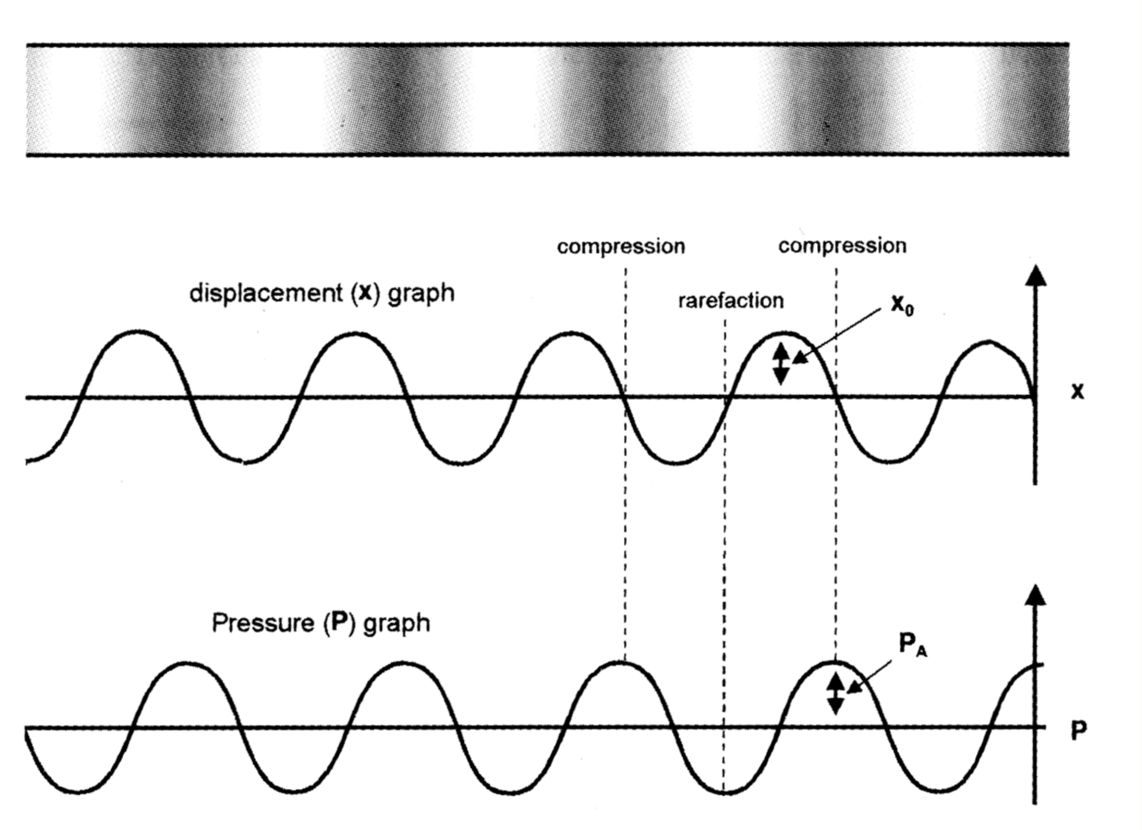
f sound frequency

$c = \lambda f$

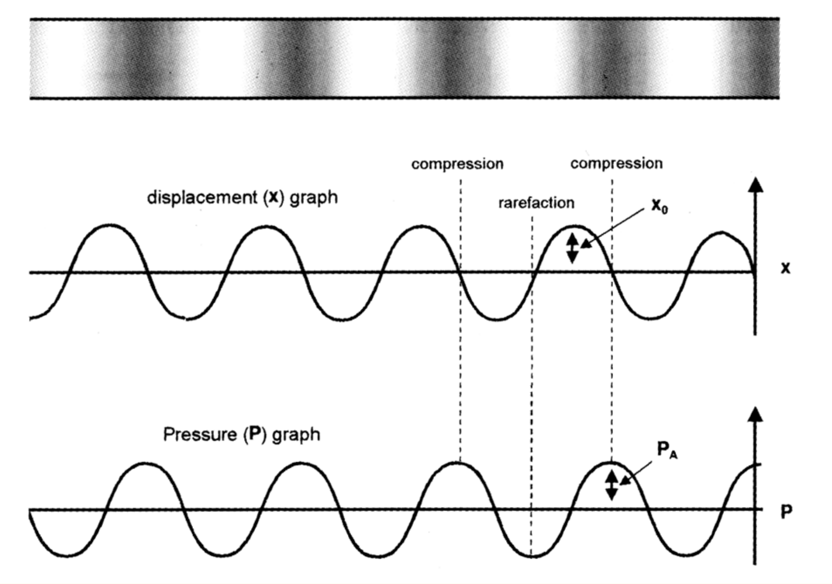
(for 20 kHz, $\lambda = 7.5$ cm)

$P_{total} = P_a + P_h$

P_h hydrostatic pressure



Acoustic Pressure



Compression and rarefaction (expansion) regions

$$P_A = \sqrt{2I\rho c}$$

P_A = driving pressure amplitude [Pa]

I = irradiation intensity [W m^{-2}]

(500 W system - 1.3 10^5 W m^{-2})

ρ = liquid density [kg m^{-3}]

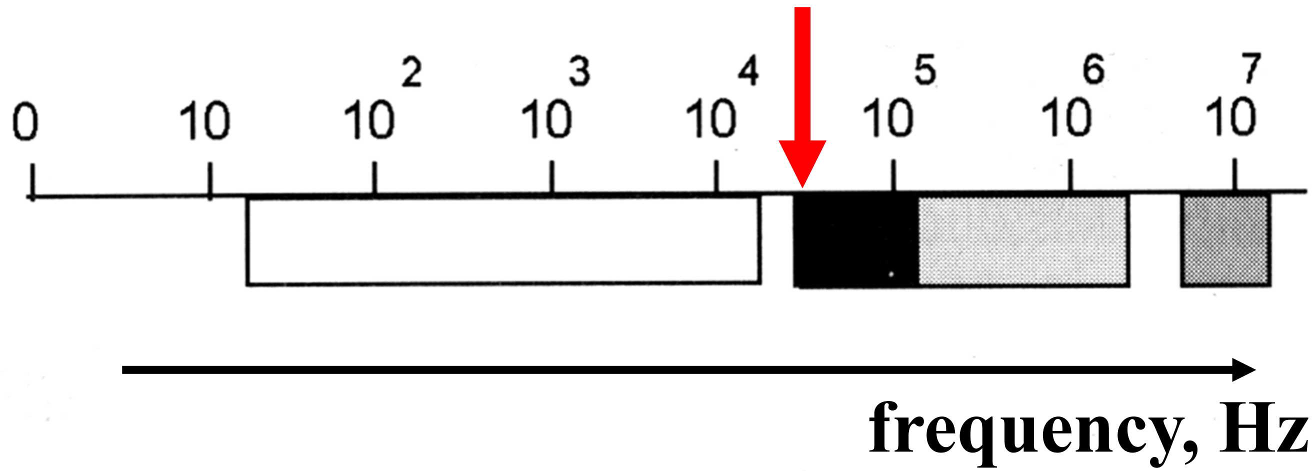
c = sound velocity in liquid [m s^{-1}]

(Water 1482 m s^{-1})

P_A = 620 700 Pa = 6.2 bar

Ultrasound

Utrasound frequencies from 20 kHz to 50 MHz



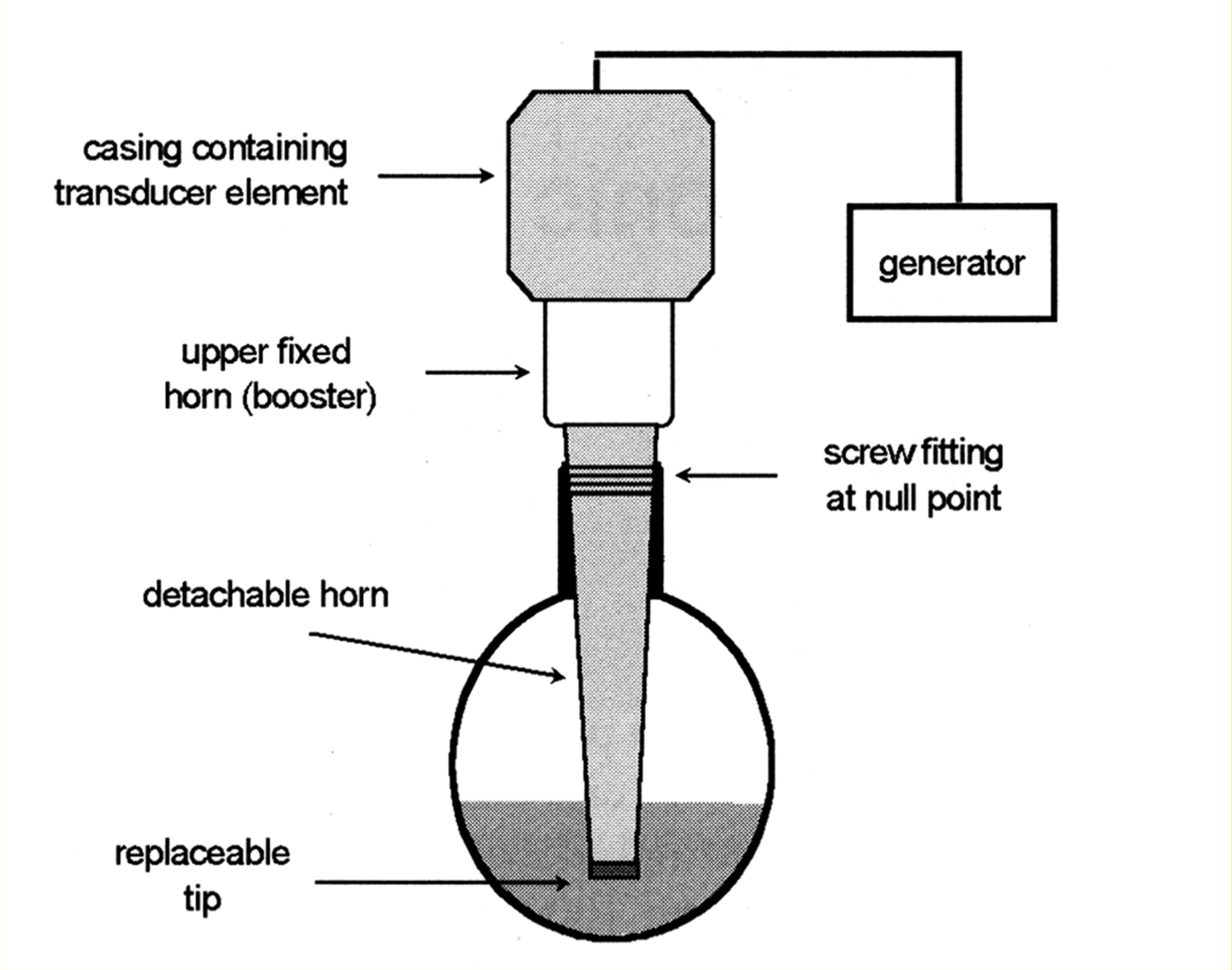
Human hearing	☐	16Hz - 18kHz
Conventional power ultrasound	■	20kHz - 100kHz
Extended range for sonochemistry	■▨	20kHz - 2MHz
Diagnostic ultrasound	▩	5MHz - 10MHz

Generation of Ultrasound

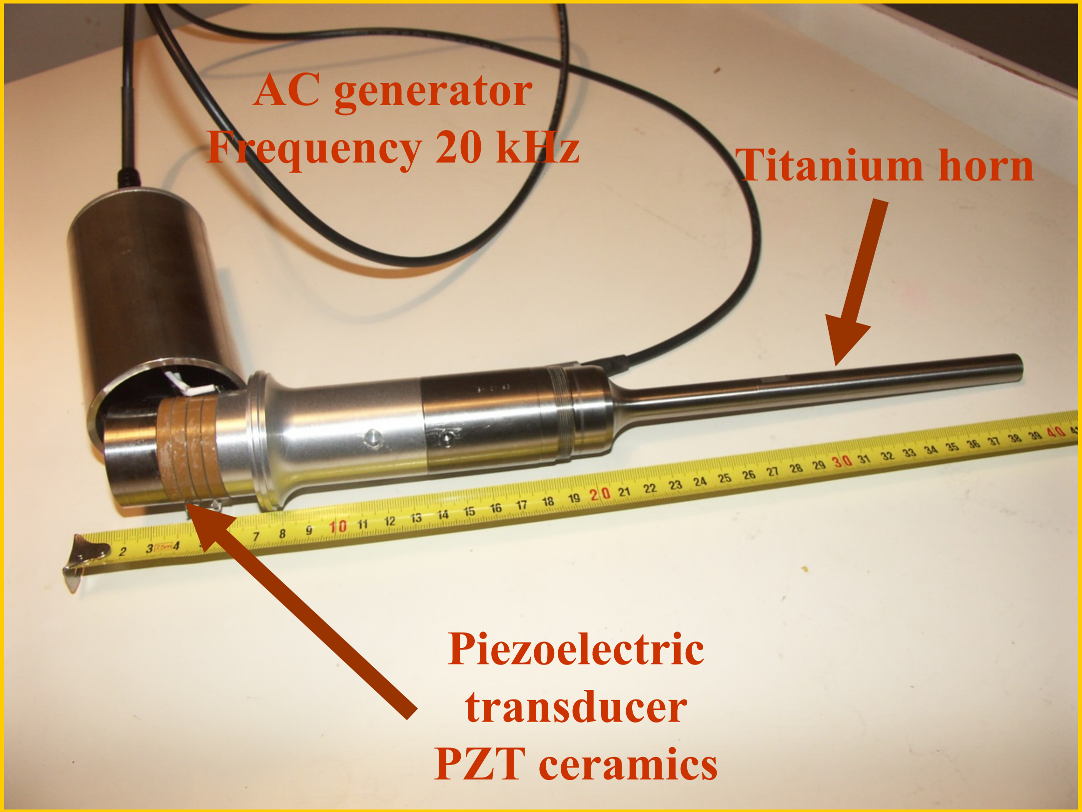
Transducer – a device converting one type of energy into another

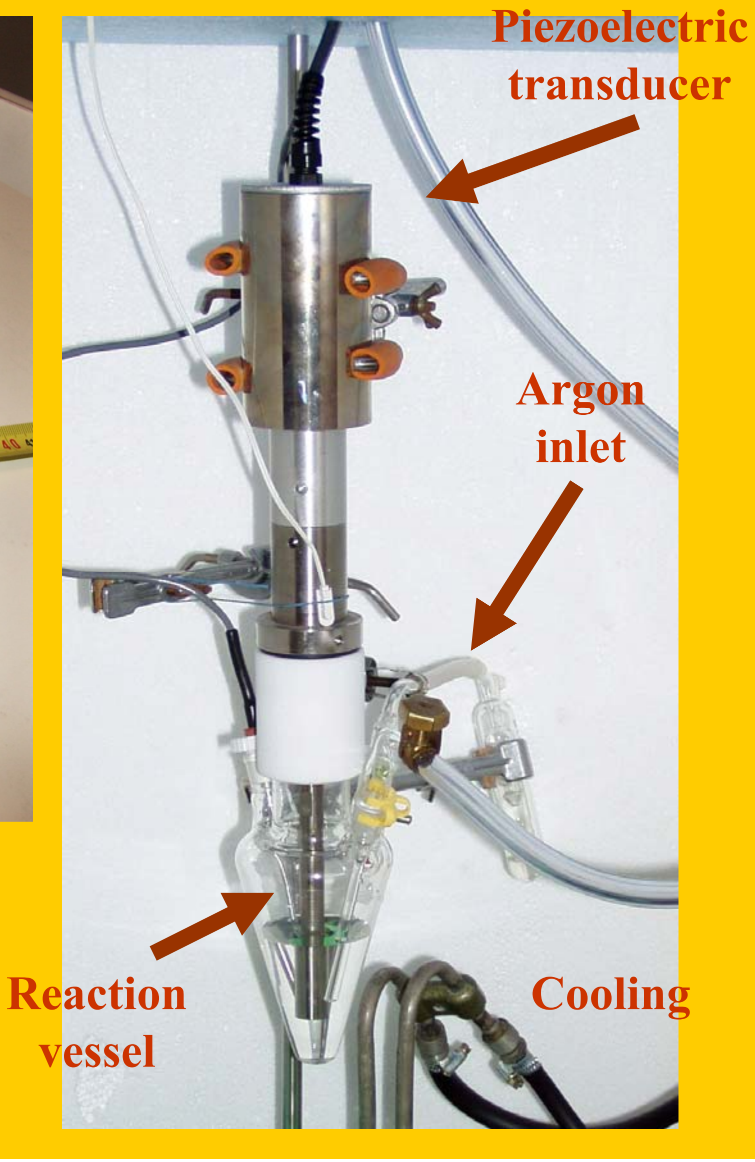
gas driven	whistle (F. Galton), liquid atomizer
	siren
liquid driven	liquid whistle homogeniser, a jet of liquid passed through an orifice on a thin metal blade, vibrations, cavitation, mixing of immiscible liquids, ketchup, mayonnaise
electromechanical	magnetostrictive, Ni, Co/Fe, Al/Fe, Tb/Dy/Fe alloys shrink when placed in mg. field, solenoid, pulses, upper limit 100 kHz, cooling
	piezoelectric, oposite charges applied on crystal sides, contraction/expansion, quartz, $Pb(Zr/Ti)O_3$ ceramics (PZT), up to MHz

Generation of Ultrasound



Sonochemical Reactor





Piezoelectric Ultrasound Generator
Ultrasound Processor VCX 500 W

Sonochemical Reactor

Ultrasound Processor VCX 500 W

Frequency 20 kHz

0 to 40 °C

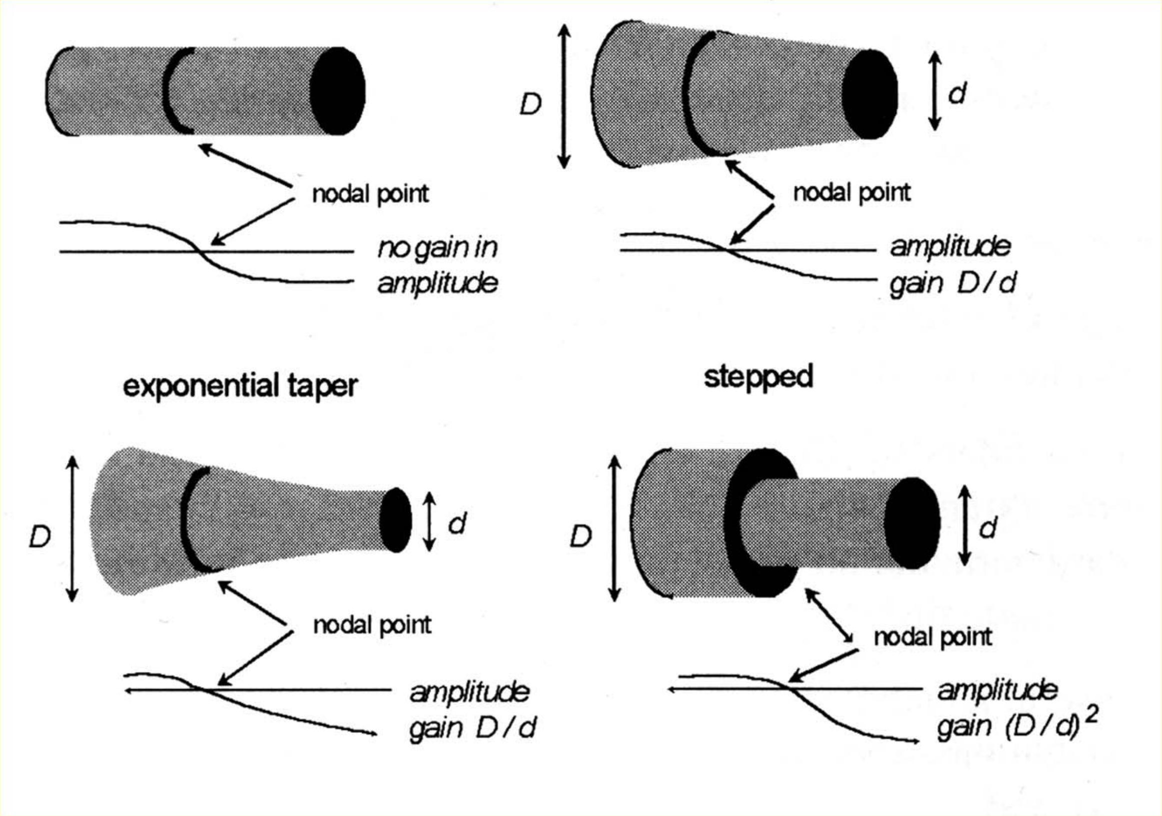
Argon (flow rate 62 cm^3 min^{-1})

TIME of ultrasound treatment
PULSE irradiation and a dwell time 2:2
TEMP maximum temperature 50 °C
AMPL amplitude 50 %

Sonochemical Reactor

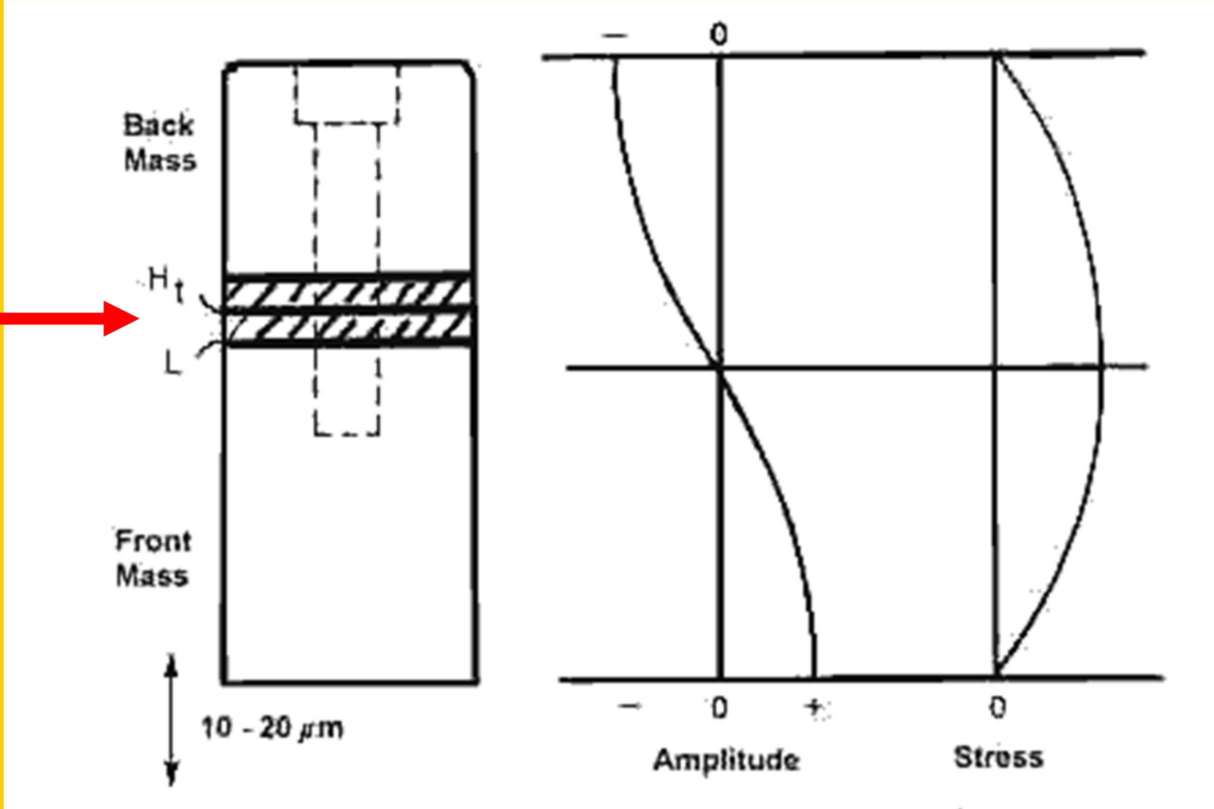
Ti alloy horn, minimum lenght is a half-wavelength of sound in a material, 26 cm for 20 kHz in Ti, multiples of 13 cm

vibration amplitude 5 - 50 μm



Sonochemical Reactor

PZT wafers



Sandwich transducer operating at 1-200 kHz

Hydrodynamic Cavitation

the passage of liquid through an orifice plate

the kinetic energy/velocity of the liquid increases at the expense of the pressure

throttling causes the pressure to fall (Bernoulli) below the threshold pressure for cavitation (vapor pressure)

cavities are generated

the liquid jet expands, the pressure recovers

energetic collapse of the cavities

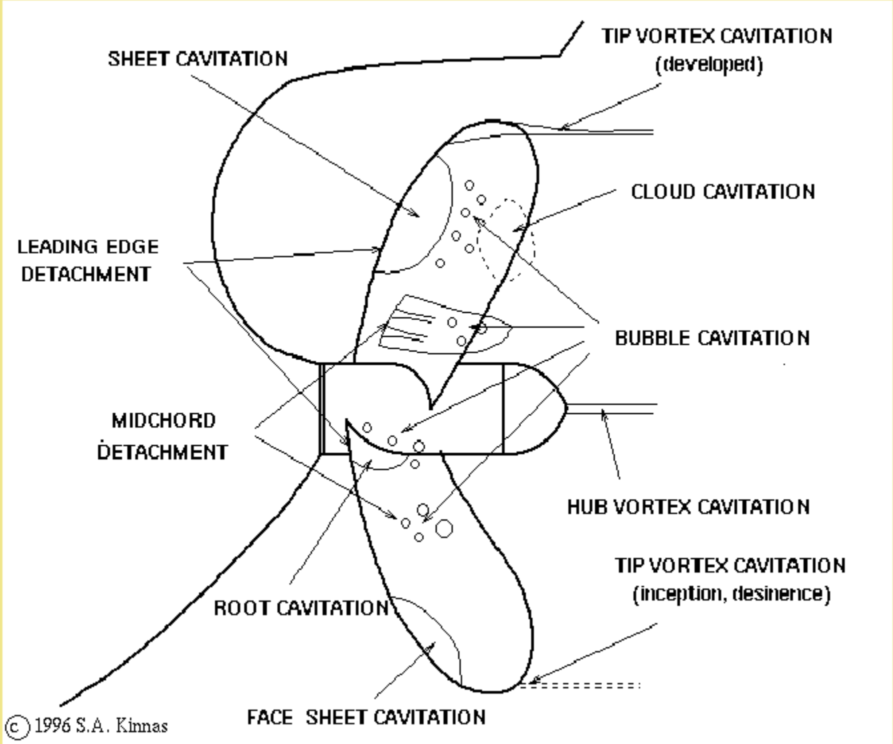
Hydrodynamic Cavitation

Lord Rayleigh for the British Admiralty 1895

cavitation erosion of propeller blades

$$R\ddot{R}+\frac{3}{2}\dot{R}^{2}=\frac{1}{\rho}[p_{g}-P_{0}-P(t)]-4\nu\frac{\dot{R}}{R}-\frac{2\sigma}{\rho R}$$

The University of Texas at Austin



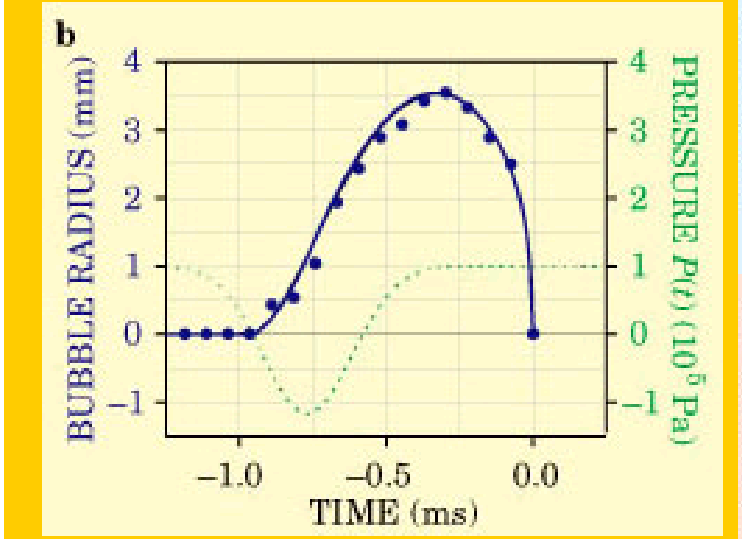
(c) 1996 S.A. Kinnas

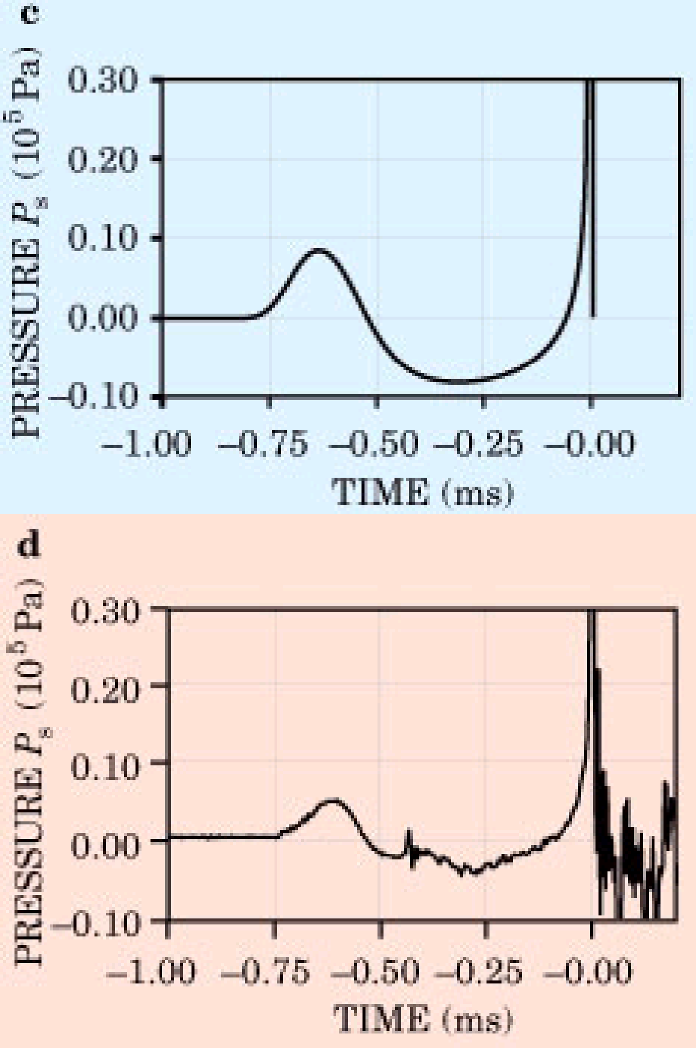
Snapping Shrimp

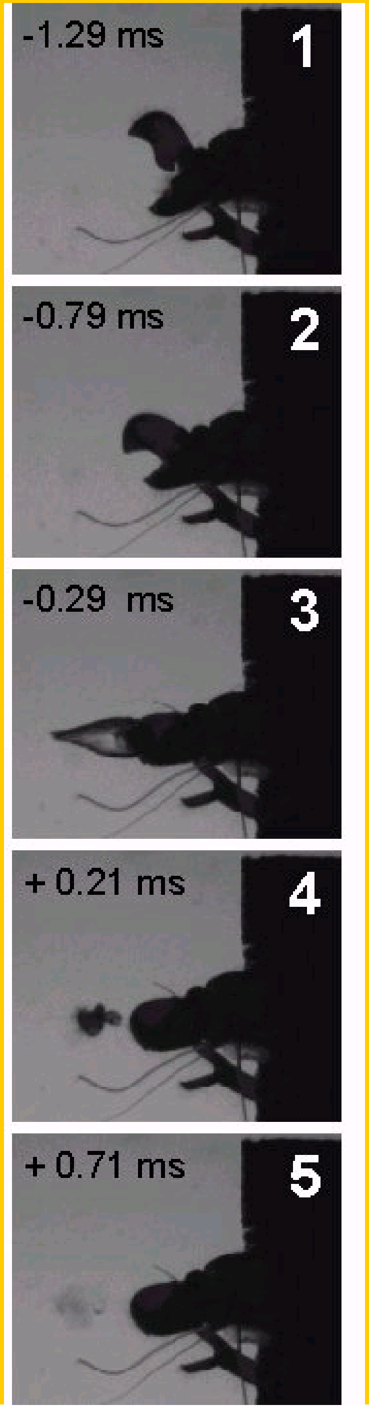
snaps a claw shut to create a water jet - speed of 30 m/s, or 100 km/h
a drop of the pressure to below the vapor pressure of water - cavitation bubbles
acoustic pressures of up to 80 kPa at a distance of 4 cm
The pressure wave is strong enough to kill small fish

M. Versluis, B. Schmitz, A. von der Heydt, D. Lohse, How Snapping Shrimp Snap: Through Cavitating Bubbles. Science 289, 2114–2117 (2000)

Snapping Shrimp

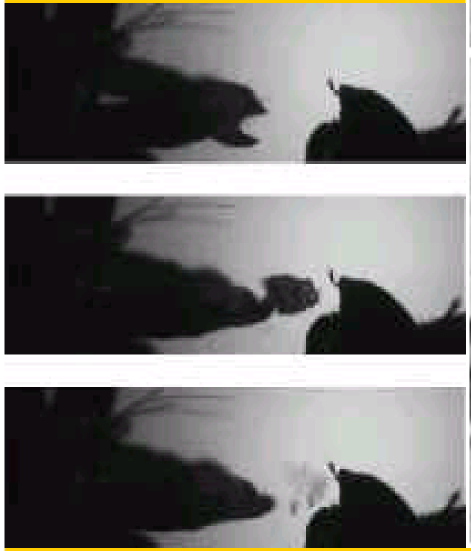


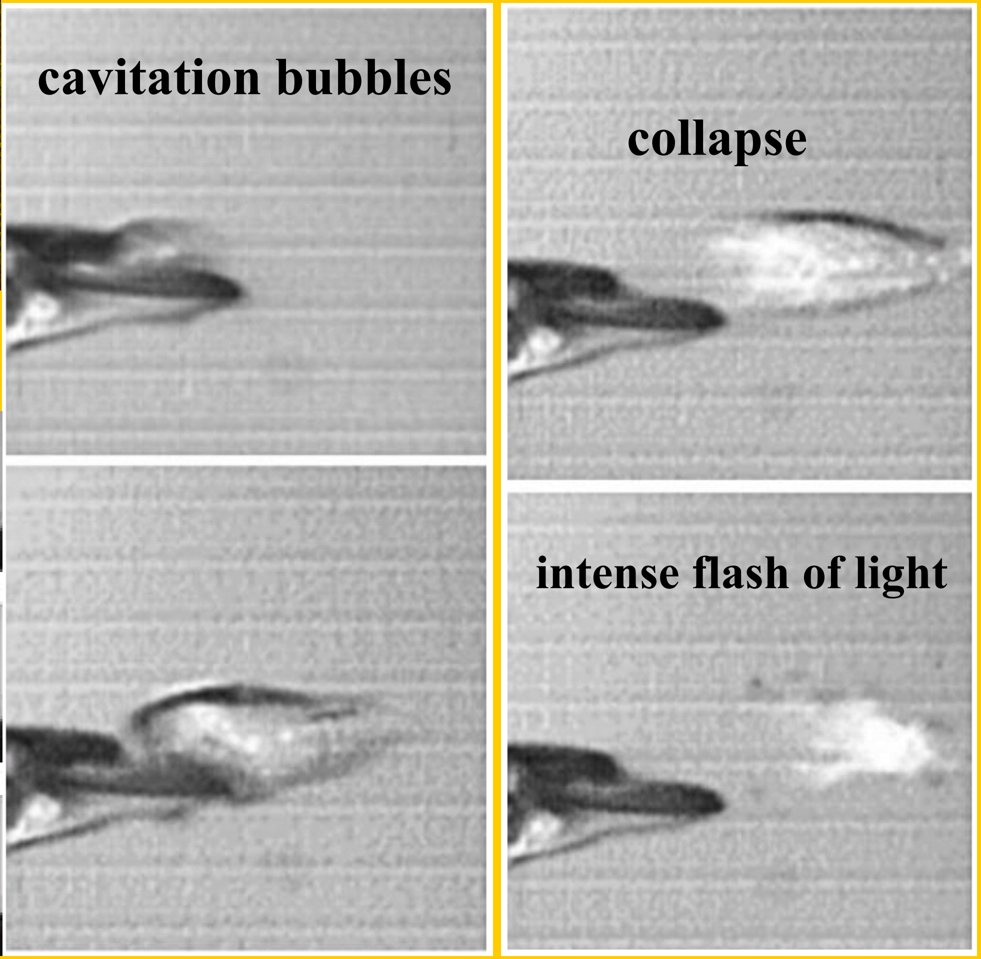


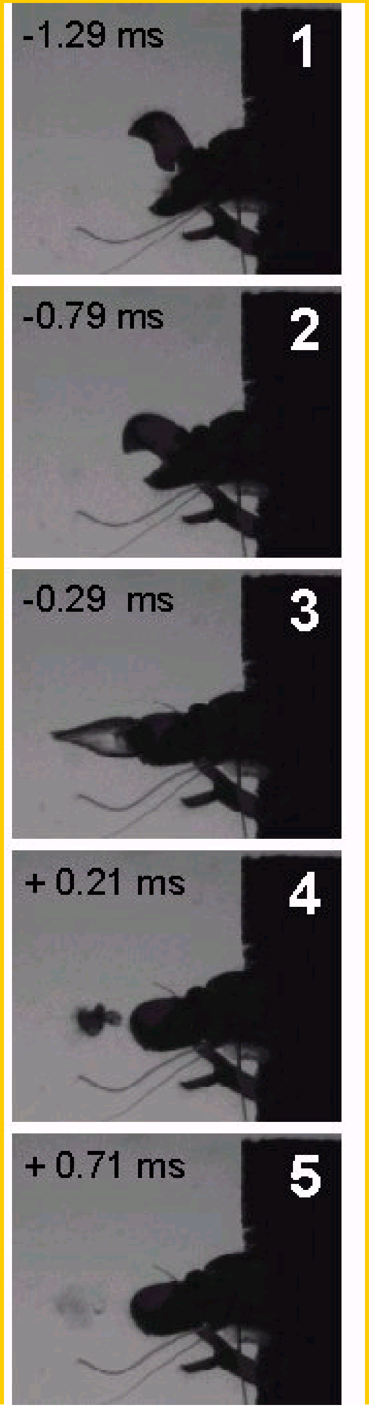


D. Lohse, B. Schmitz, M.Versluis, Nature 413, 477-478 (2001)

Snapping Shrimp

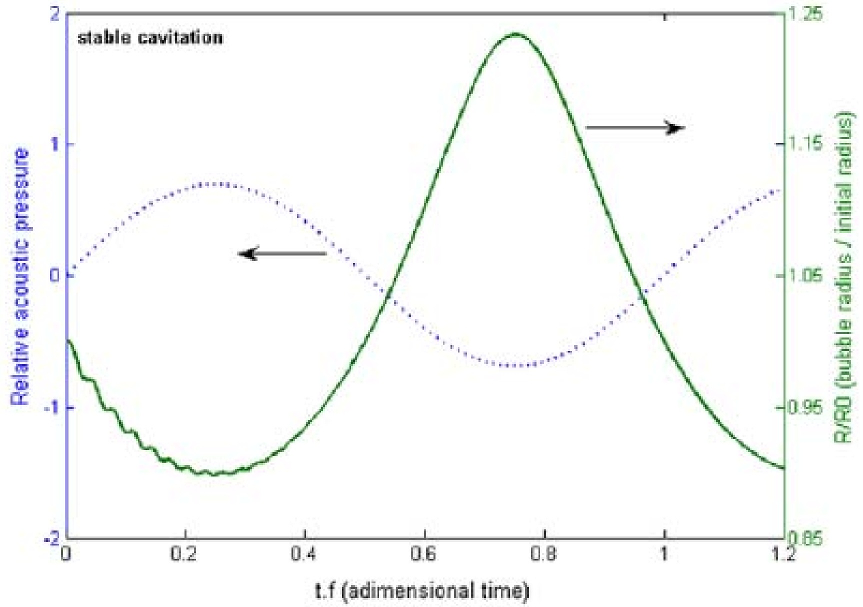


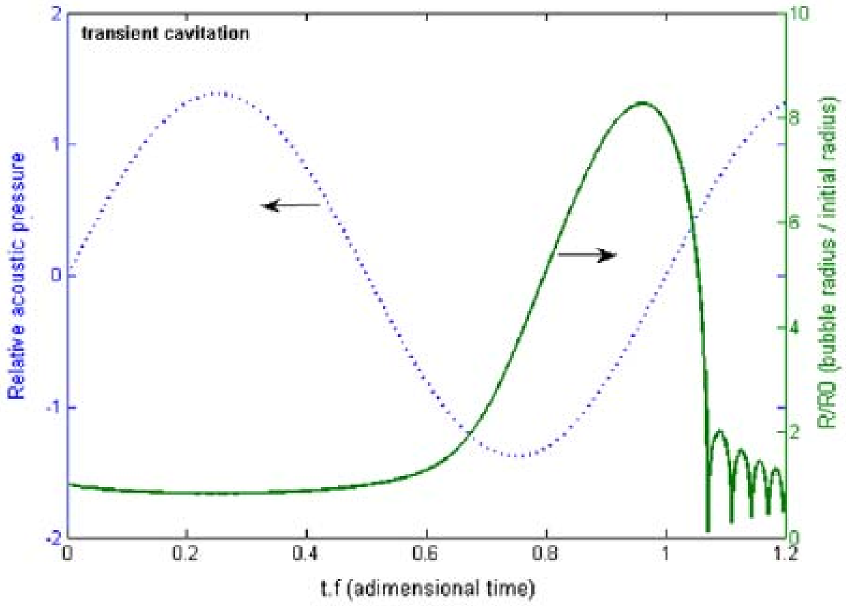




D. Lohse, B. Schmitz, M.Versluis, Nature 413, 477-478 (2001)

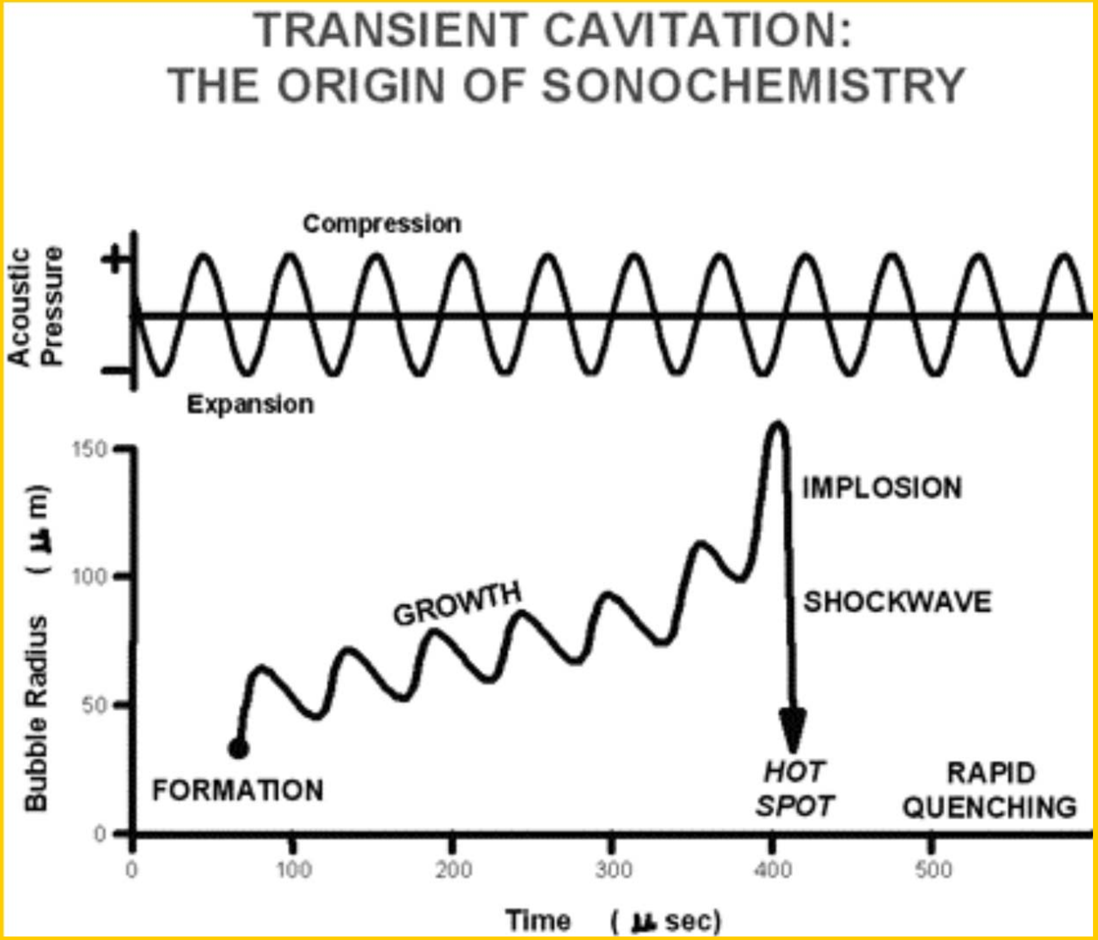
Stable vs. Transient Cavitation

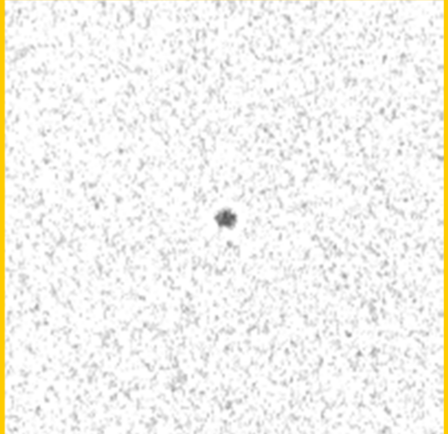




Acoustic Cavitation

Cavitation effects = creation, growth, and implosive collapse of bubbles (1-2 µs) in a liquid = implosion HOT SPOT (1 ns)





stable cavitation - bubbles oscillate for many cycles

transient cavitation - transient cavities expand rapidly collapse violently

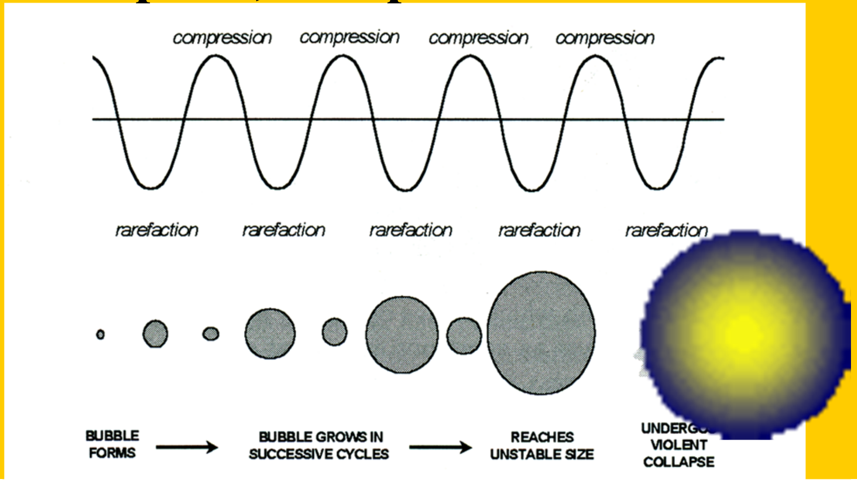
Acoustic Cavitation

Cavitation effects = creation, growth, and implosive collapse of bubbles in a liquid

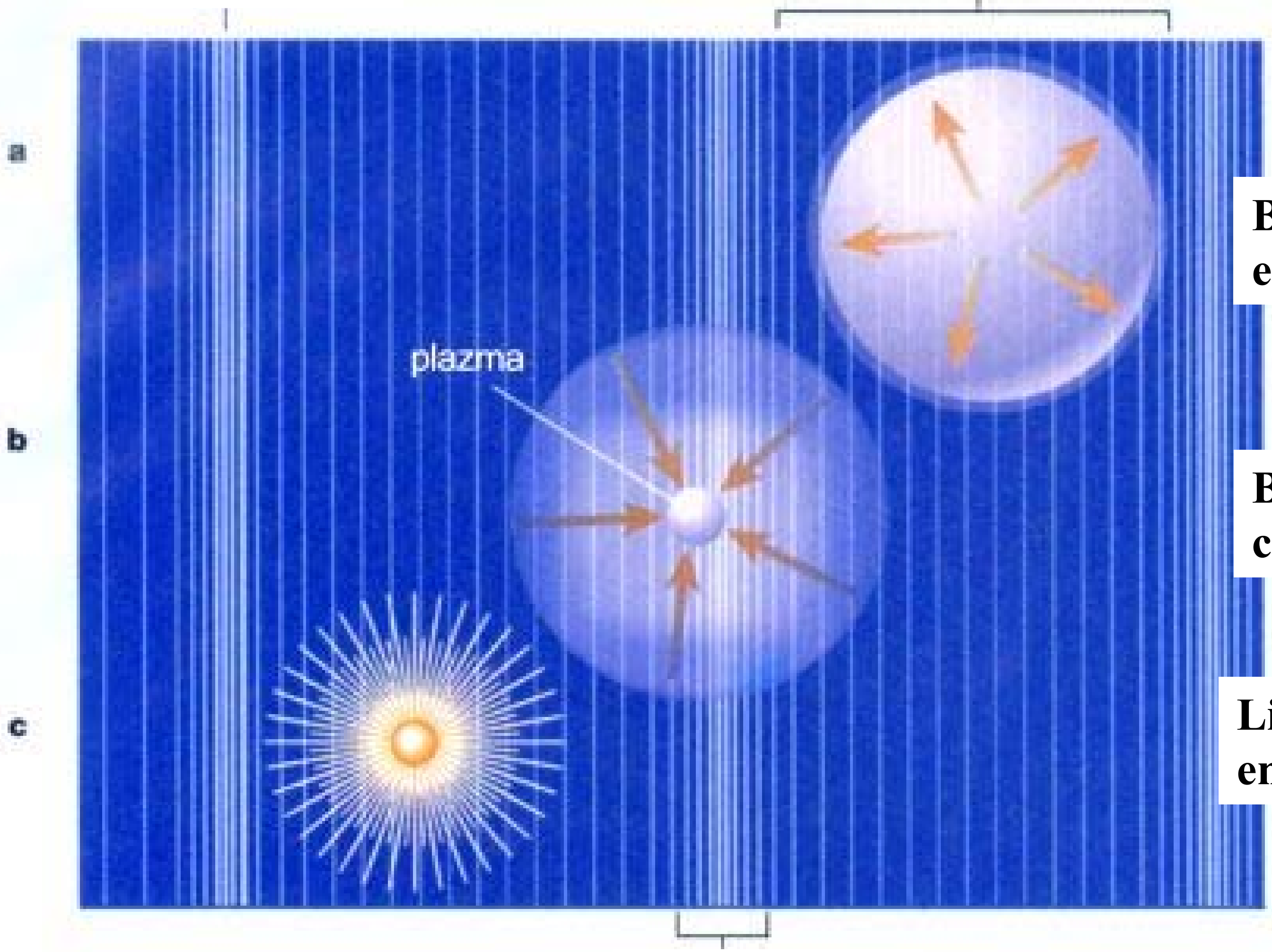
Bubble formation = breakage of liquid during **expansion**, overcoming tensile strength (pure water 1500 bar, only 6.2 bar available)

Weak spots needed = dissolved gas molecules, solid particles, trapped gases

Bubble growth (300 µs), energy absorption, size oscillations
critical size (170-300 µm) = most efficient energy absorption, rapid growth, inefficient energy absorption, collapse



Acoustic Cavitation



Standing wave

Low pressure

Bubble expansion

Bubble collapse

Light emisssion

High pressure

Acoustic Cavitation

Bubbles collapse = spherically symmetrical implosion,
shear forces, adiabatic compression, life time 1-2 µs

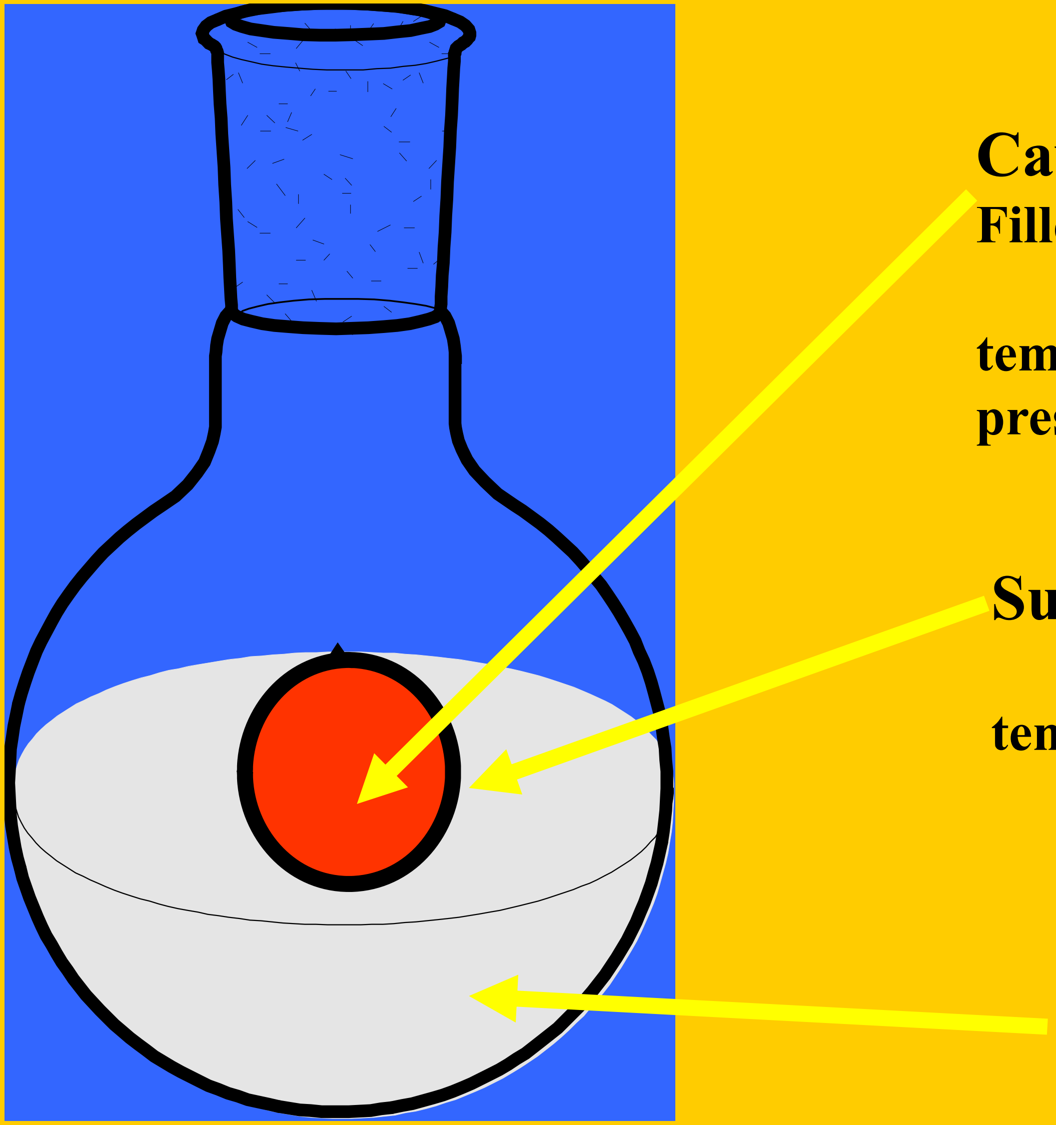
Hot spot = end of the collapse
temperature of the gas inside bubble
5 000 – 20 000 °C (for 1 ns)

surrounding liquid layer 2000 °C

pressure 500 – 1500 bar

Extreme cooling rates 10^{10} K s^{-1}
red hot steel poured into water 2500 K s^{-1}

Homogeneous Sonochemistry
Two-Site Mechanism



Cavity interior

Filled with gases and vapors

temperatures 5 000 – 20 000 °C
pressure 500 – 1500 bar

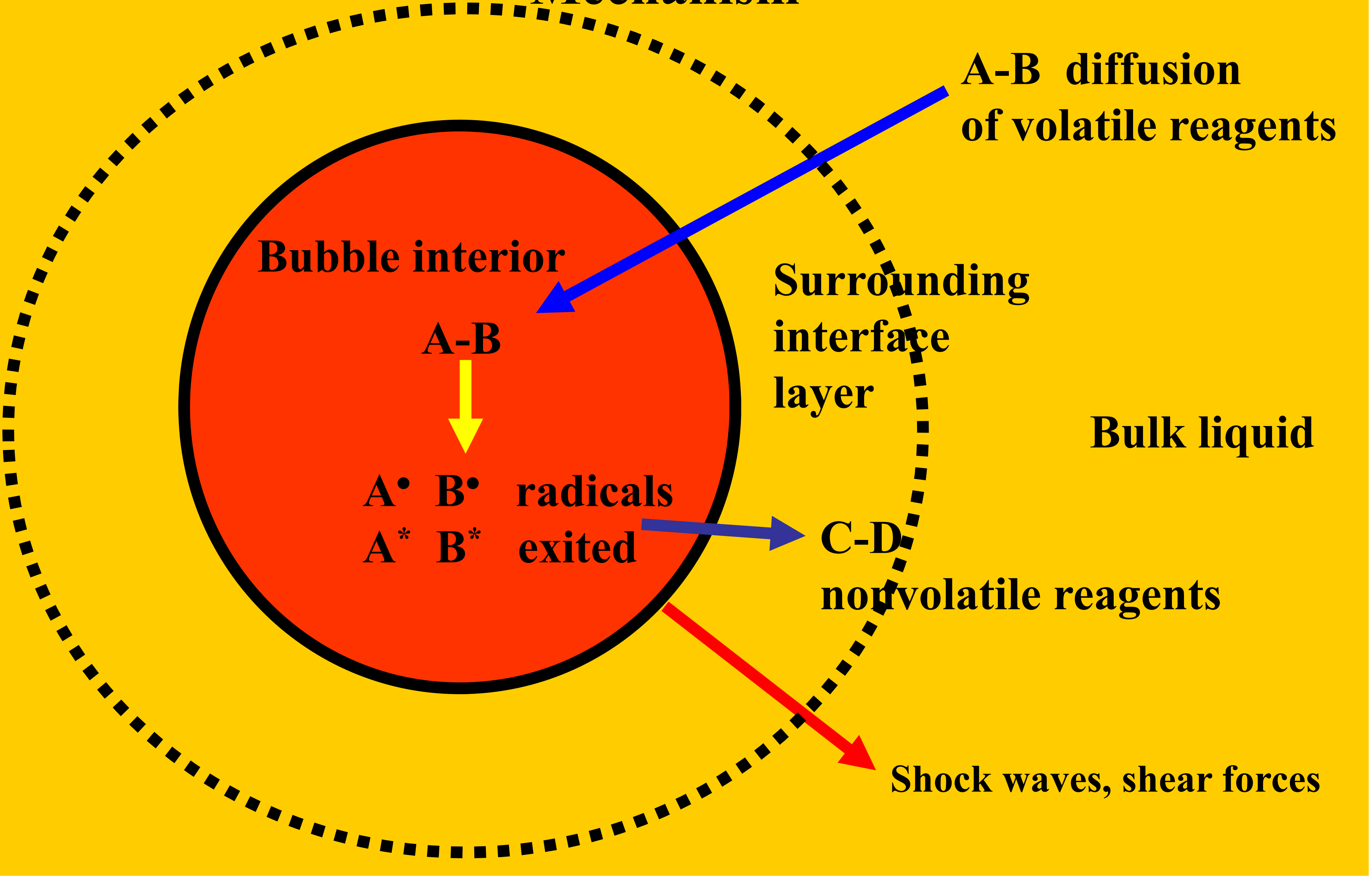
Surrounding liquid layer

temperatures 2000 °C

Bulk liquid

Shock waves, shear forces

Homogeneous Sonochemistry Mechanism



A-B diffusion
of volatile reagents

Bubble interior

A-B

$A^\bullet$ $B^\bullet$ radicals
A^* B^* exited

Surrounding
interface
layer

Bulk liquid

C-D
nonvolatile reagents

Shock waves, shear forces

How to Measure the Temperature inside a Bubble ?

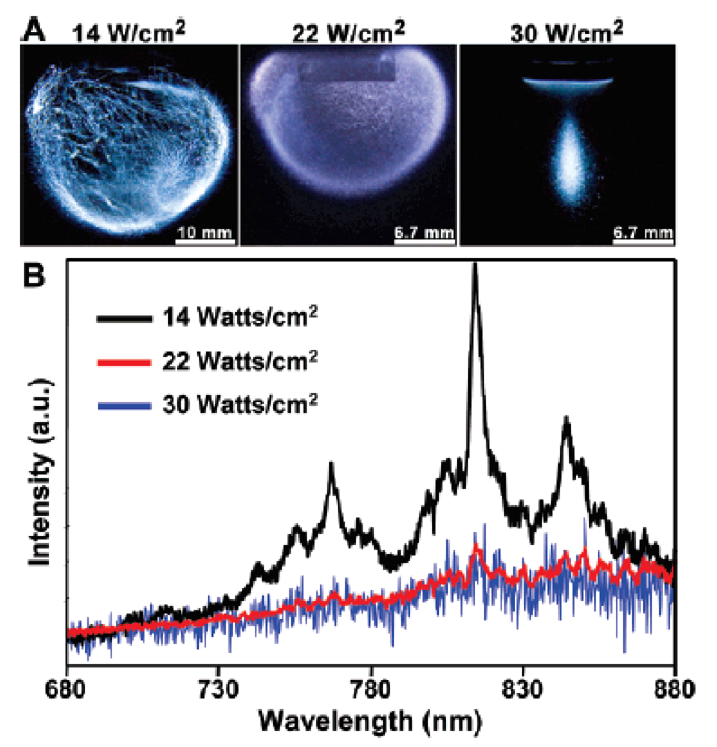
Sonoluminescence - Light generated during the implosive collapse of bubbles in liquids irradiated with ultrasound

Kenneth S. Suslick
University of Illinois

95% H_2SO_4(aq.)
under Ar
20 kHz (14 W/cm^2)
Ti horn directly immersed
T = 298 K

- **Apparent blackbody temperature**
- **Ar emission**
- **SO and O_2^+ emission**

8 000 – 15 000 K



Temperature/Pressure inside a Bubble
Neppiras Equation

$$T_{\max} = T_0 \frac{P_a(\gamma - 1)}{Q} \qquad P_{\max} = Q\left(\frac{P_a(\gamma - 1)}{Q}\right)^{\frac{\gamma}{\gamma - 1}}$$

P_a = acoustic pressure

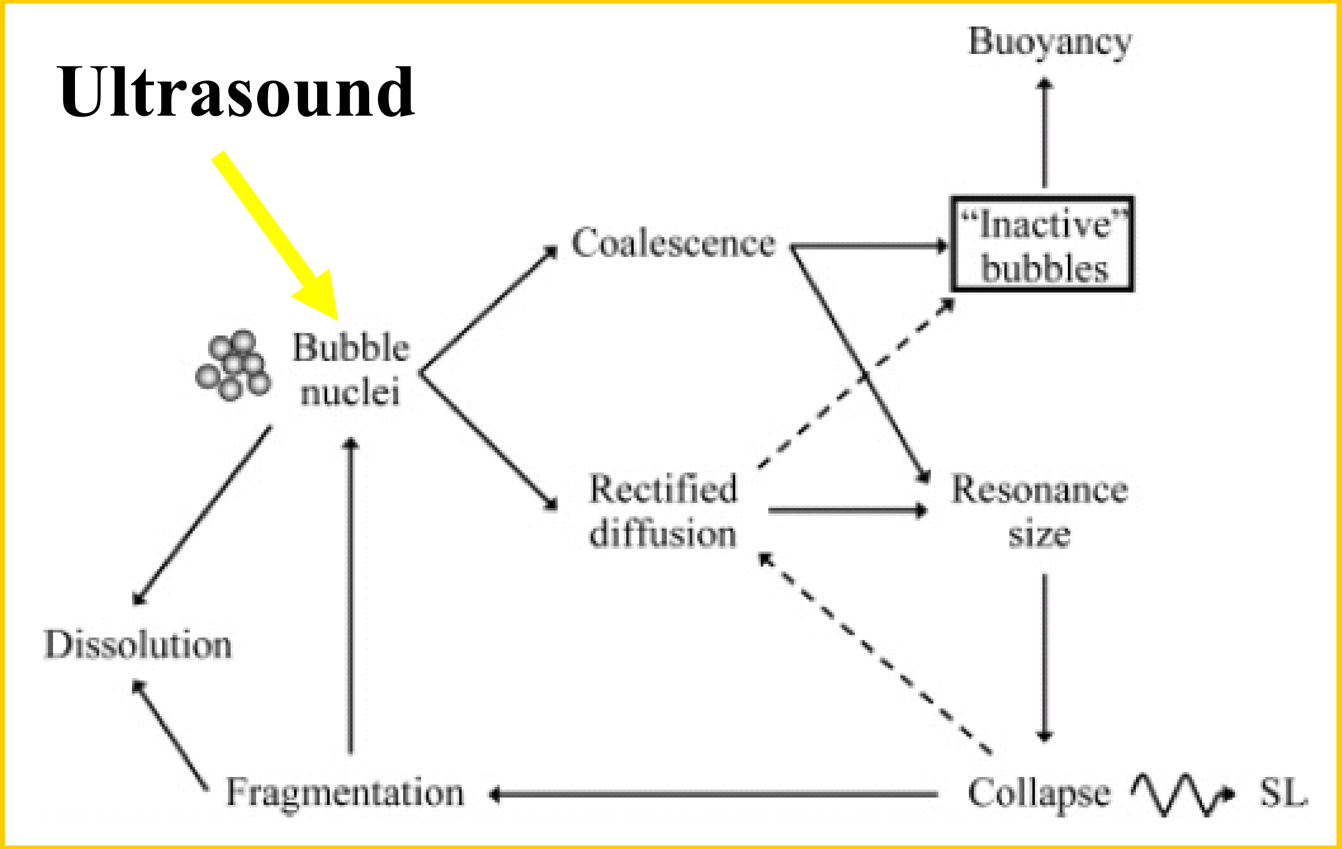
T_0 = solution temperature

$\gamma = C_p/C_v$

Q = gas pressure inside a bubble upon initiation of the collapse, at its maximum size

Gas	**$\gamma = C_p/C_v$**
Kr	**1.66**
Ar	**1.66**
He	**1.63**
O_2	**1.41**

Fate of Bubbles under Ultrasonic Irradiation



Rectified diffusion – during expansion phase the bubble has larger surface area – more gas diffuses inside than during compression gets out

Single Bubble Sonoluminescence
SBSL

D. F. Gaitan, L. A. Crum, 1990

a method to trap a single sonoluminescing bubble within an acoustic standing wave field

Standing acoustic wave field

One bubble trapped

The bubble oscillates for many cycles

Bubble sonoluminescence

Single Bubble Sonoluminescence
SBSL

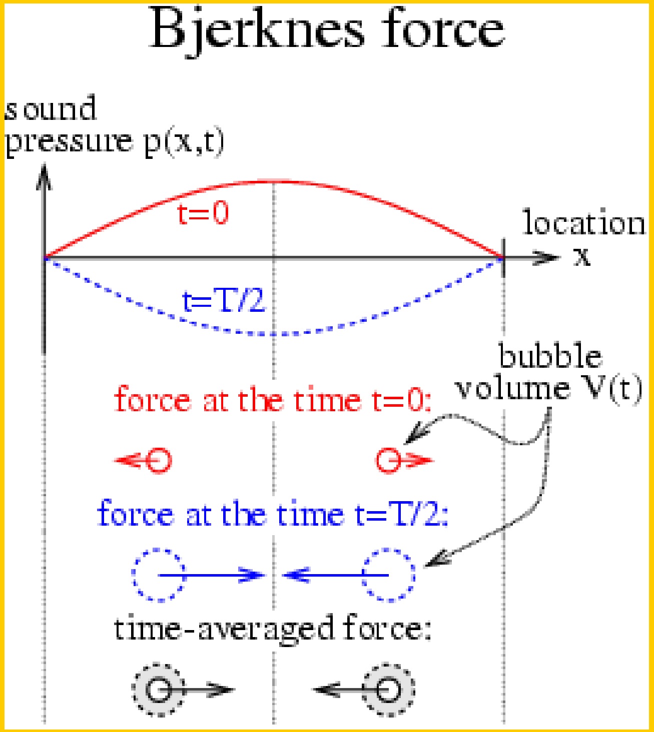
D. F. Gaitan, L. A. Crum, 1990

Standing acoustic wave field 1 bar

One bubble levitates in the acustic field

The bubble oscillates for many cycles

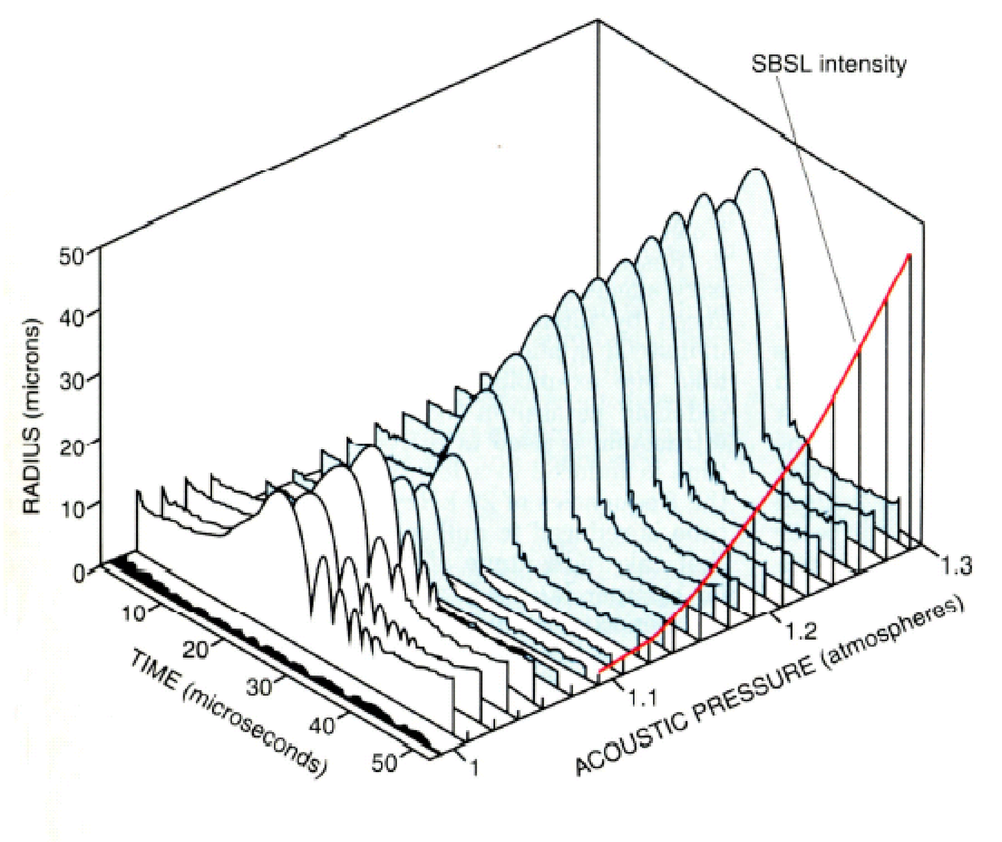
Bubble sonoluminescence



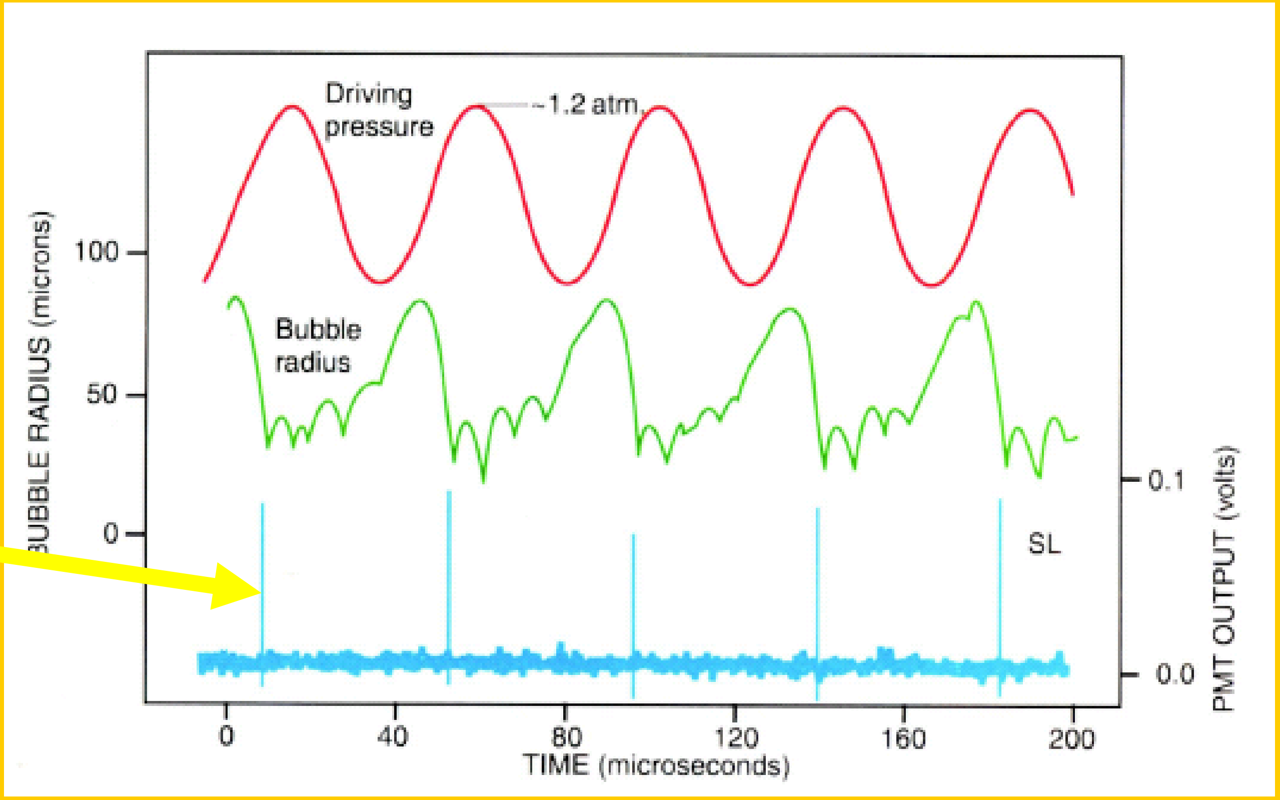
C. A. and V. Bjerknes
The force on an object in a liquid depends on its volume and the pressure gradient, the time averaged force drives the bubble towards the antinode of sound pressure and keeps it there.

Single Bubble Sonoluminescence
SBSL

Proper conditions for a single sonoluminescing bubble within an acoustic standing wave field



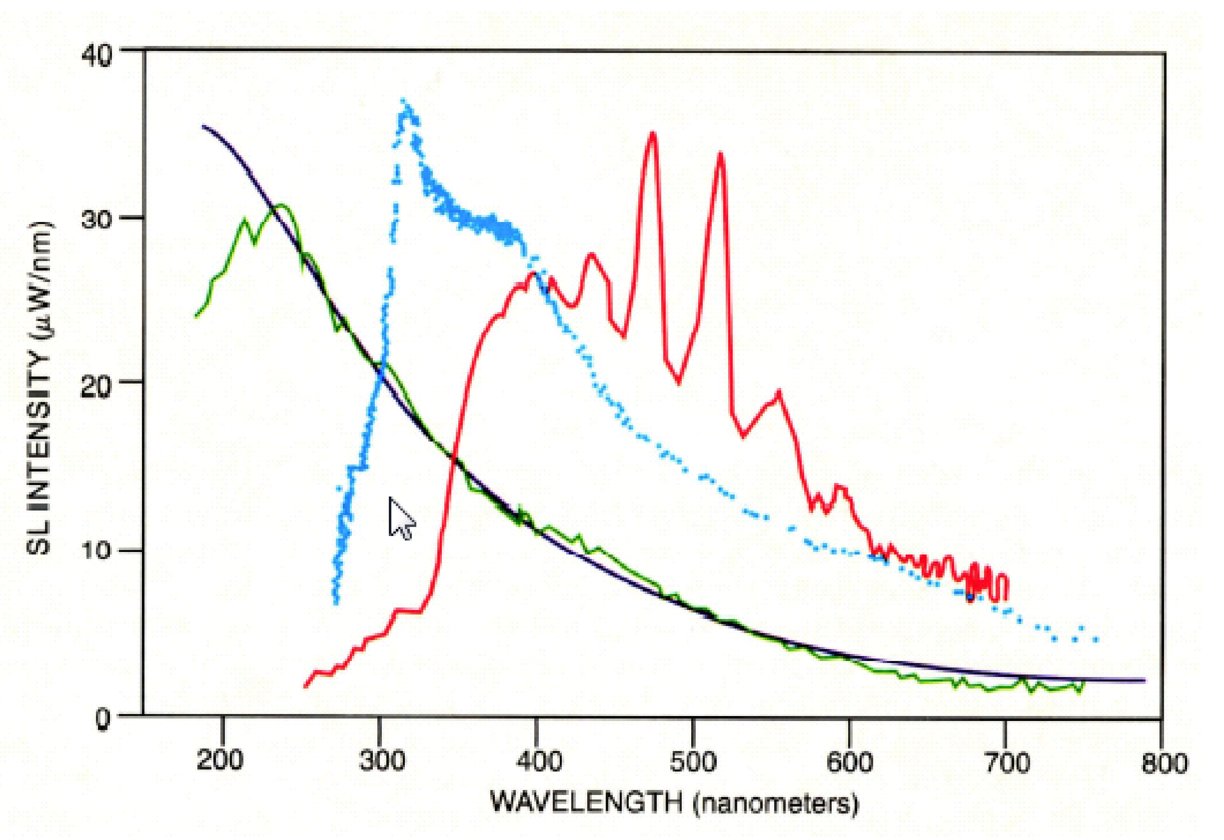
Single Bubble Sonoluminescence
SBSL



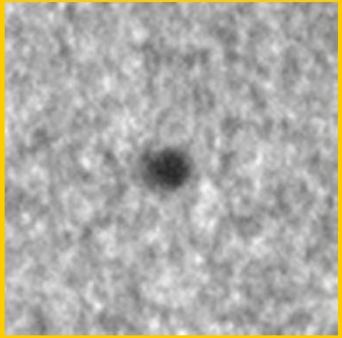
**Sonoluminescence
Pulses 50 ps**

Single Bubble Sonoluminescence
SBSL

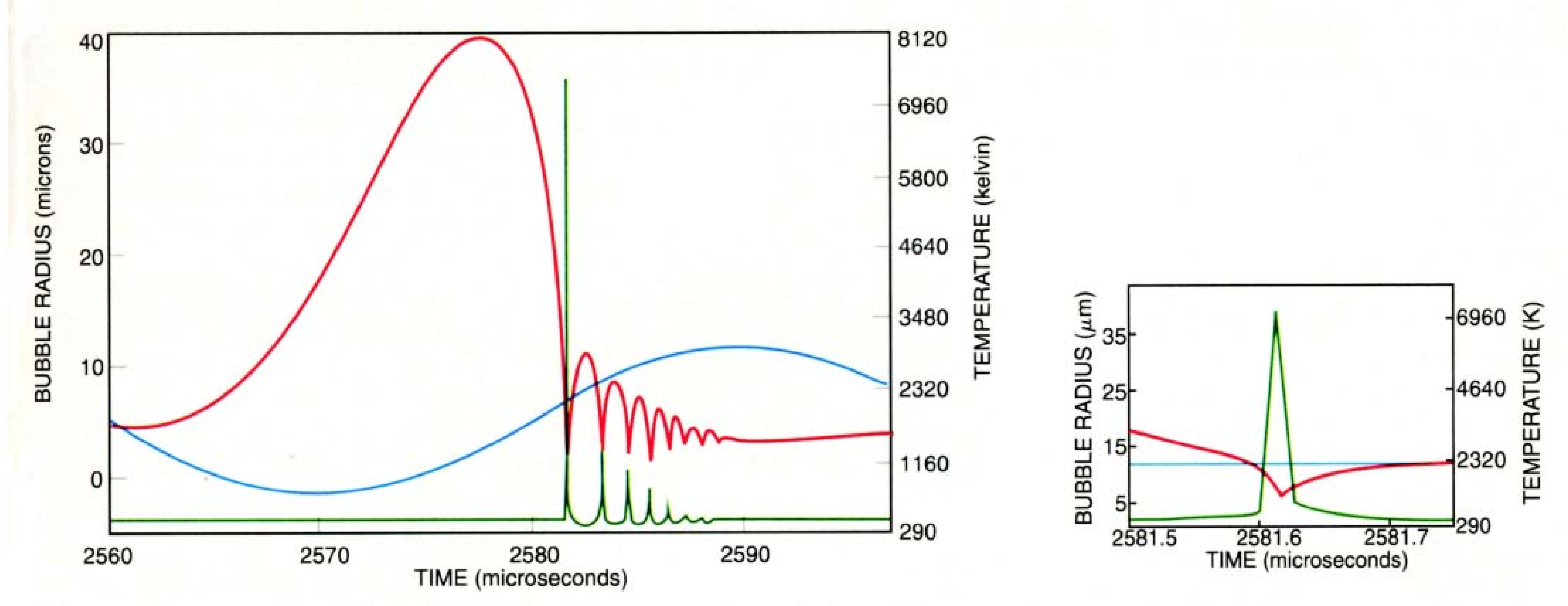
Red – MBSL in dodecane
Blue – MBSL in water, 16 kHz
Green – SBSL in water, 43 kHz
Black – blackbody curve for 16200 K



Single Bubble Sonoluminescence
SBSL



Red - bubble radius
Green - bubble temperature
Blue - acoustic pressure 1.3 bar/25 kHz



Multi Bubble Sonoluminescence
MBSL

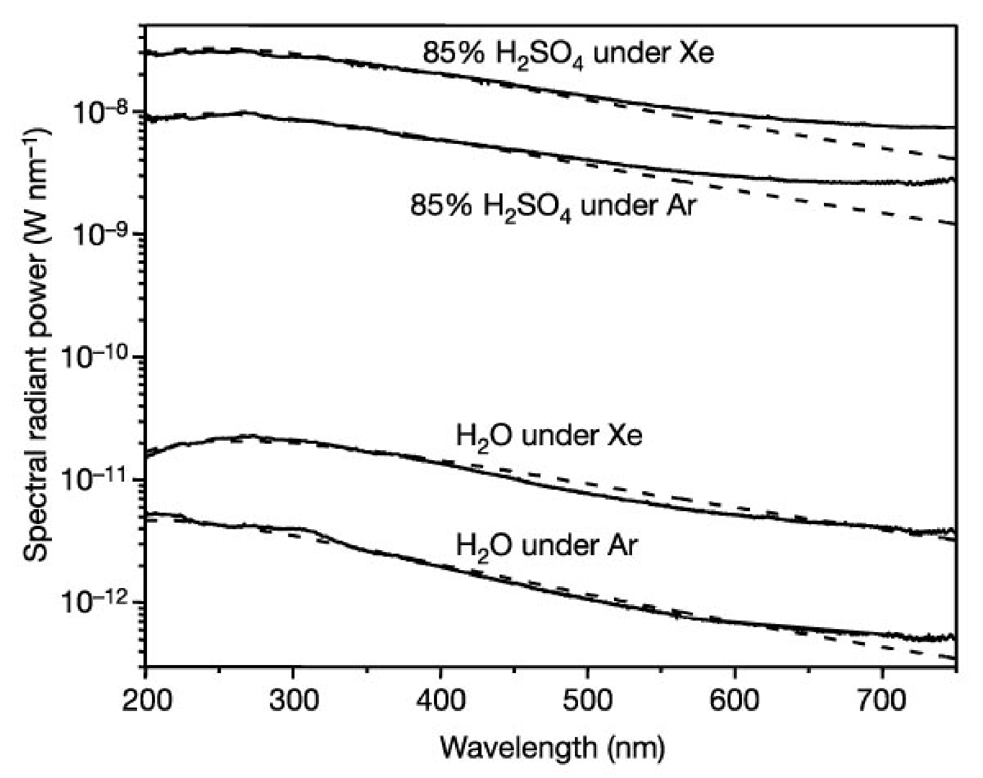
Multi-bubble sonoluminescence

Spatial and temporal average

250 bar

Sonoluminescence

Light generated during the implosive collapse of bubbles in liquids irradiated with ultrasound



Apparent blackbody temperature
(all 4 spectra)

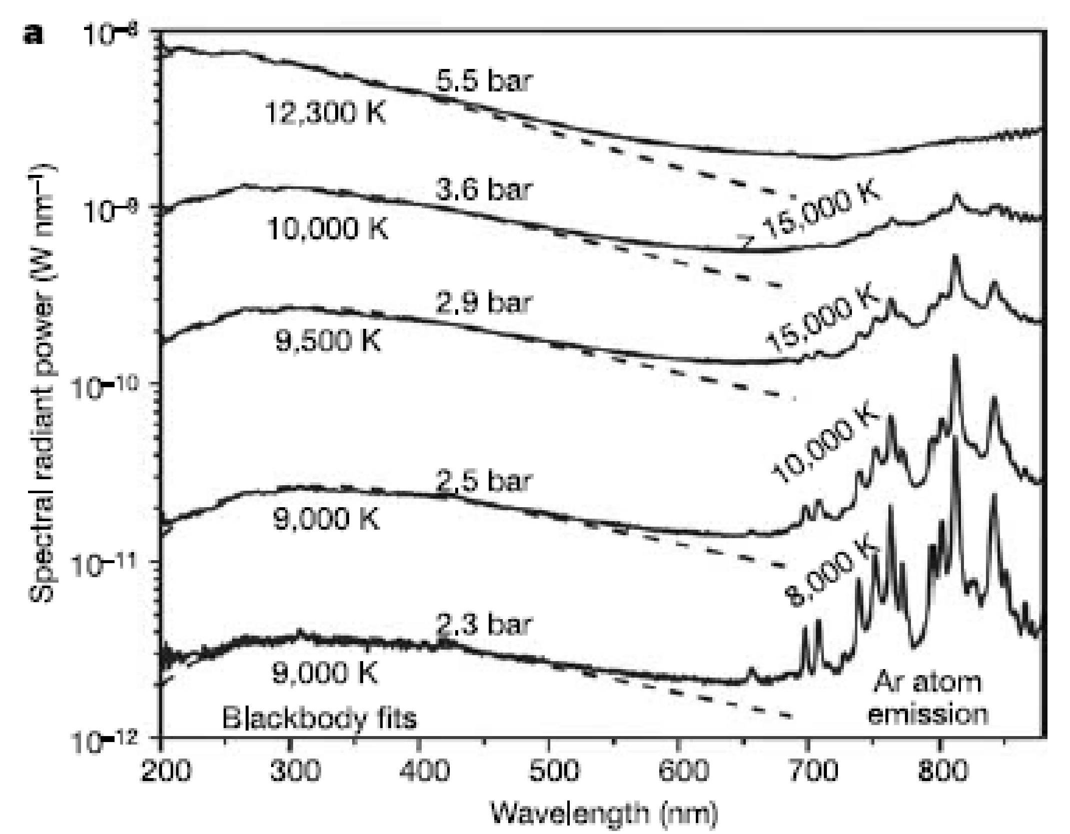
12500 ± 1500 K

Sonoluminescence

95% H_2SO_4(aq.)

blackbody temperature

Ar emission

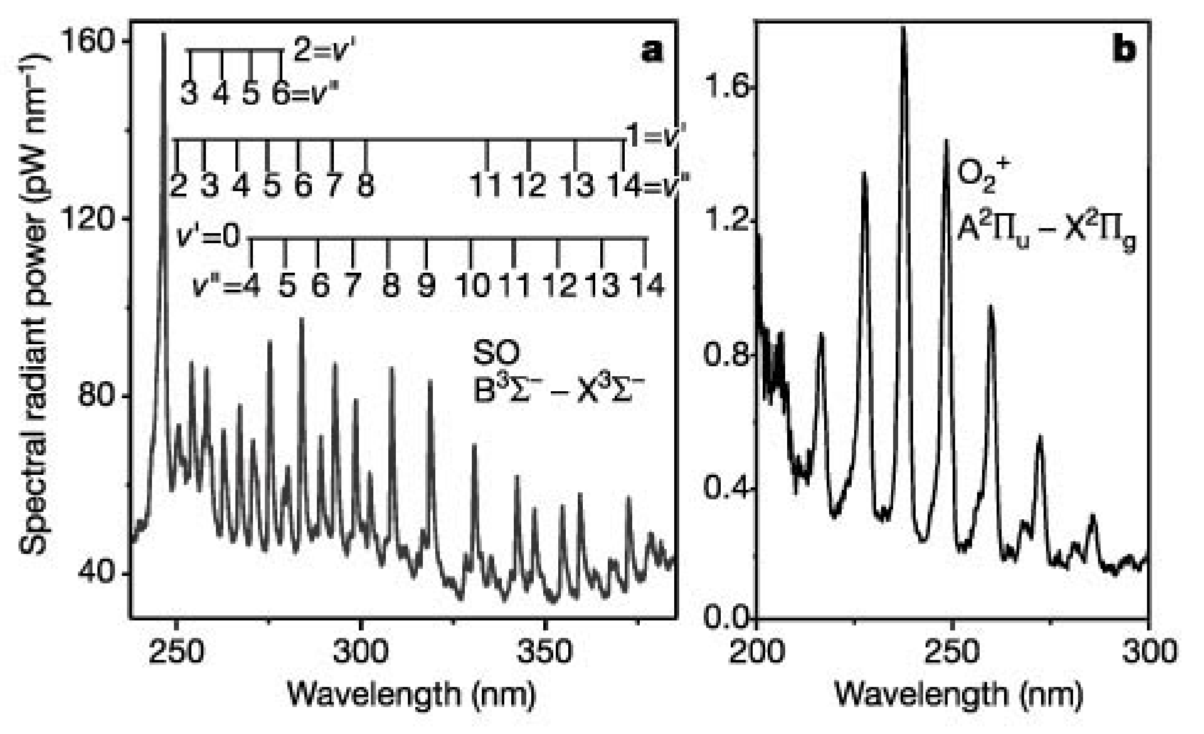


an optically opaque plasma core

Sonoluminescence

95% H_2SO_4(aq.)

SO and O_2^+ emission
with vibronic progression



1580 ± 110 K at 3.3 bar

2470 ± 170 K at 4.2 bar

3480 ± 240 K at 5.1 bar

Sonofusion Fraud

$$\mathrm{D}+\mathrm{D}\rightarrow {}^{3}\mathrm{He}(0.82MeV)+\mathrm{n}(2.45MeV)$$

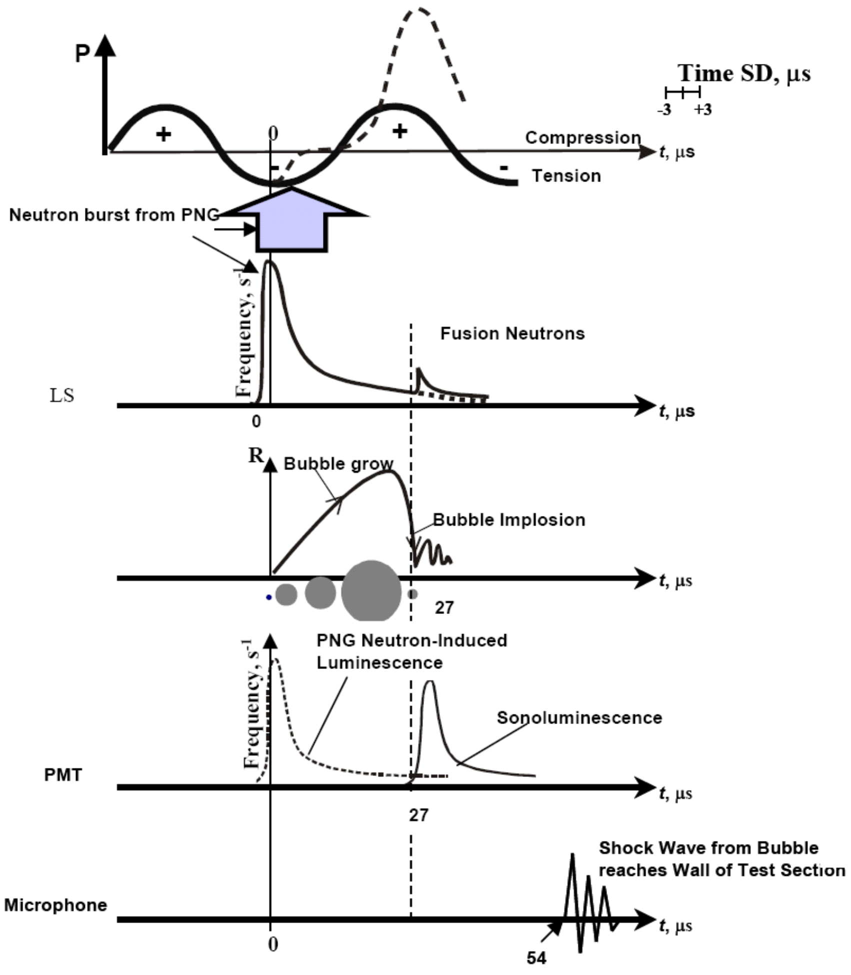
$$\mathrm{D}+\mathrm{D}\rightarrow \mathrm{T}(1.01MeV)+\mathrm{H}(3.02MeV)$$

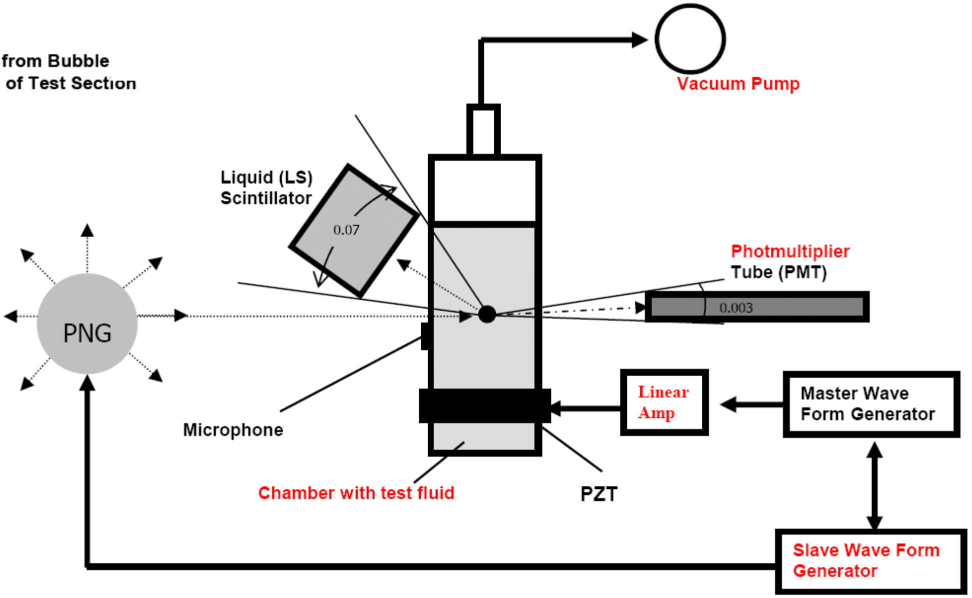
Sonofusion Fraud

Degassed deuterated acetone

$(CD_3)_2CO$, 0 °C

$4\ 10^5$ neutrons s^{-1}





Power Measurement in Sonochemistry

Calorimetry

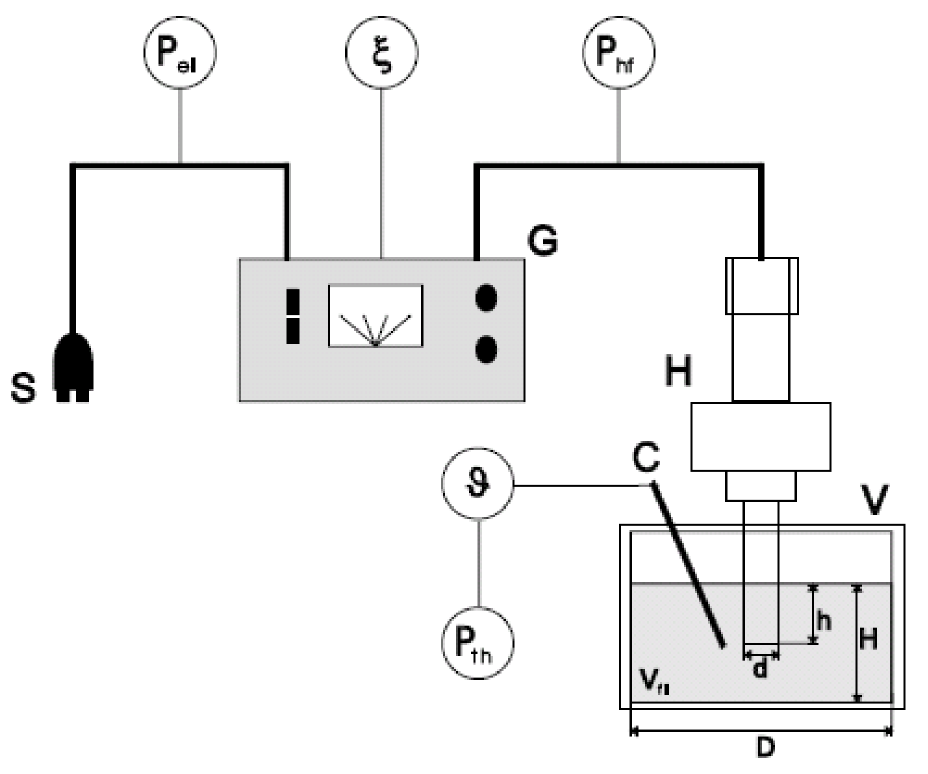
P = power, W

P el = input power to generator

P hf = high-freq. power output

P th = power input into liquid

$$P_{th} = \frac{dT}{dt} c_p m$$



Power Measurement in Sonochemistry

Calorimetry

P = power, W
T = temperature, K
t = time, s
c_p = heat capacity, J g^{-1} K^{-1}

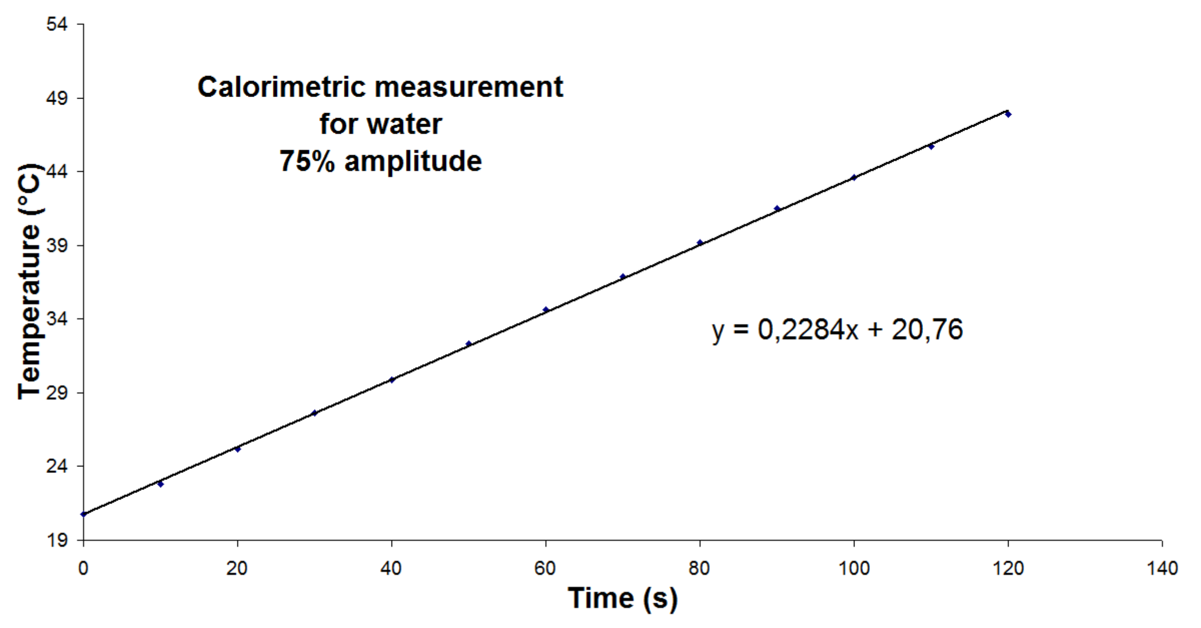
m = mass, g

$$P = \frac{dT}{dt} c_p m$$

Volume 50 cm^3
Argon atmosphere
Error 5%

heat capacity, J g^{-1} K^{-1}

Water	4.2
Tetraglyme	2.08



Power Measurement
in Sonochemistry

Chemical dosimetry

The Weissler reaction

$$CCl_4 + H_2O \longrightarrow Cl_2 + CO + 2\ HCl$$

$$2\ KI + Cl_2 \longrightarrow I_2 + 2\ KCl$$

$$I_2 + 2\ S_2O_3^{2-} \longrightarrow 2\ I^- + S_4O_6^{2-}$$

Volume 50 cm^3
KI 0.1 M
CCl_4 0.2 cm^3
Time 30 min

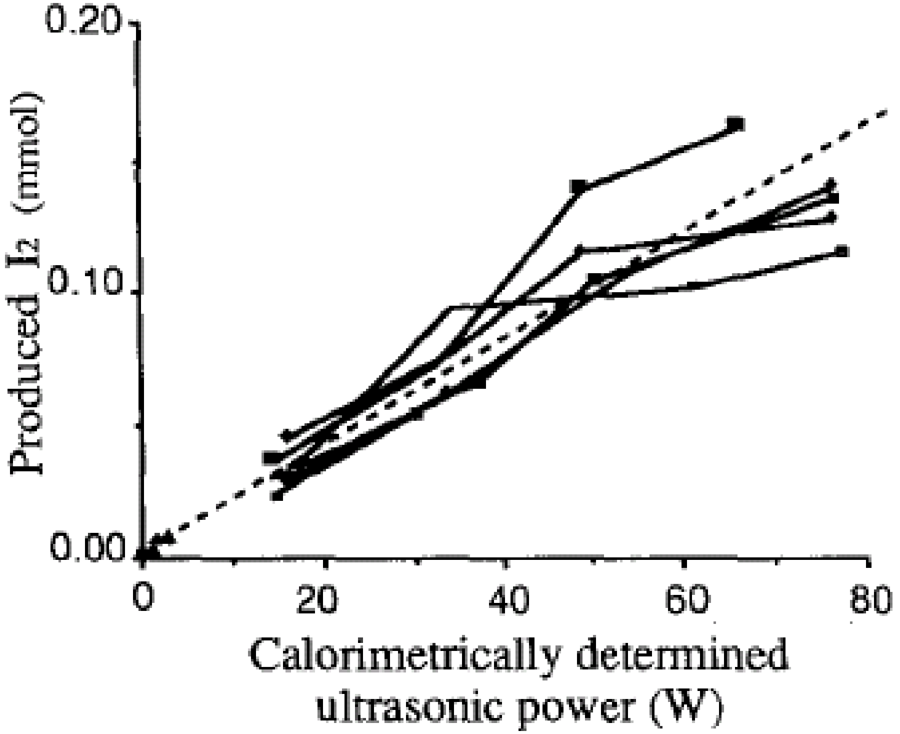
I_3^-
λ_{max} = 355 nm
ε = 26303 dm^3 mol^{-1} cm^{-1}

Weissler Reaction

$CCl_4 + H_2O \longrightarrow Cl_2 + CO + 2\,HCl$

$2\,KI + Cl_2 \longrightarrow I_2 + 2\,KCl$

$I_2 + 2\,S_2O_3^{2-} \longrightarrow 2\,I^- + S_4O_6^{2-}$



Power Measurement in Sonochemistry

Chemical dosimetry

The Fricke reaction

$$H_2O \longrightarrow H^{\cdot} + OH^{\cdot}$$

$$Fe^{2+} + OH^{\cdot} \longrightarrow Fe^{3+} + OH^{-}$$

Volume 50 cm^3
$(NH_4)\ Fe(SO_4)_2.6H_2O$
0.001 M

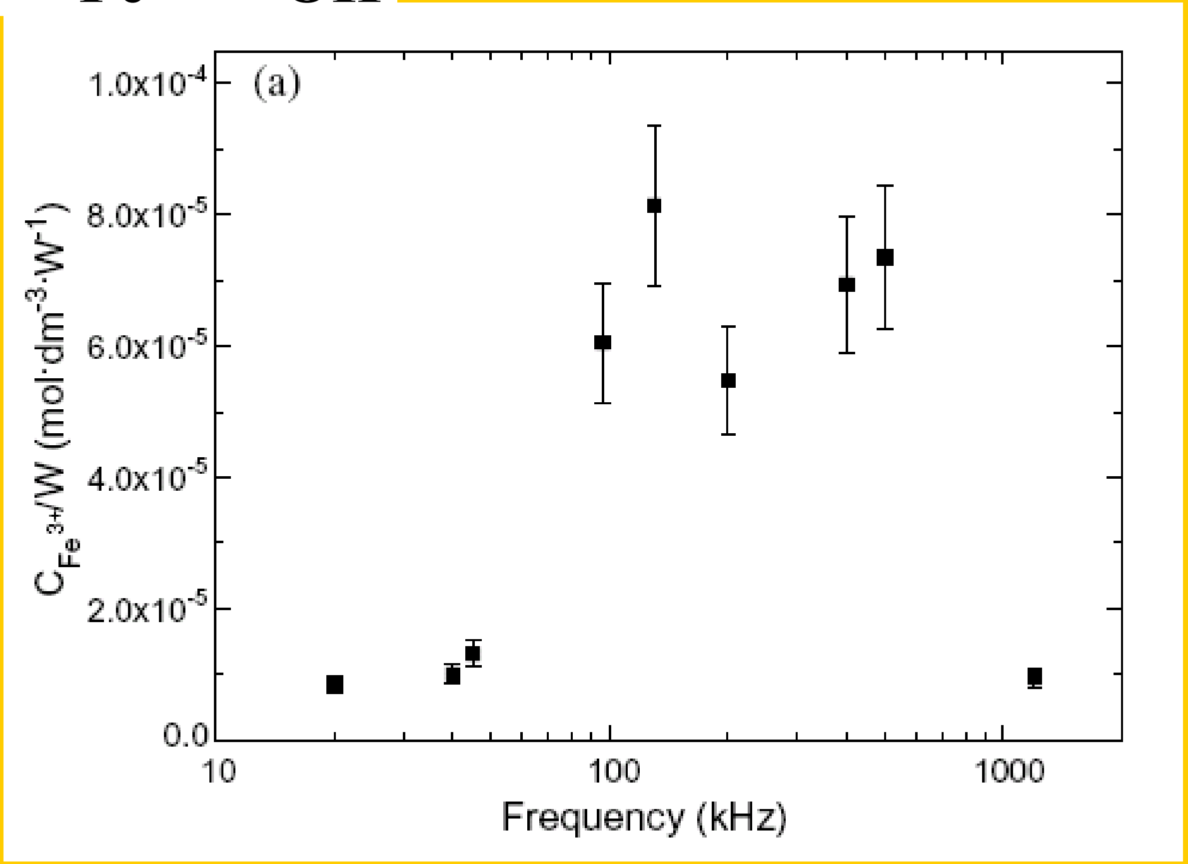
H_2SO_4 0.4 M
NaCl 0.001 M
Time 30 min

Fe^{3+}
$\lambda_{max} = 304$ nm
$\varepsilon = 2197\ dm^3\ mol^{-1}\ cm^{-1}$

Fricke Reaction

$H_2O \longrightarrow H^{\cdot} + OH^{\cdot}$

$Fe^{2+} + OH^{\cdot} \longrightarrow Fe^{3+} + OH^{-}$

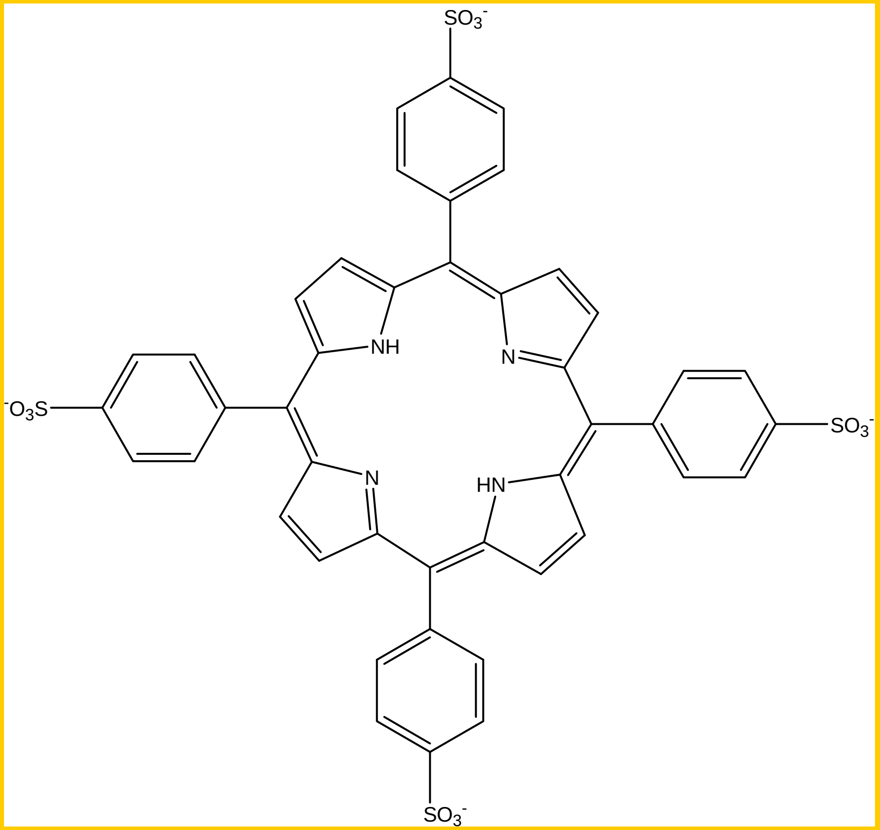


Power Measurement in Sonochemistry

Chemical dosimetry

Porphyrin decomposition ratio

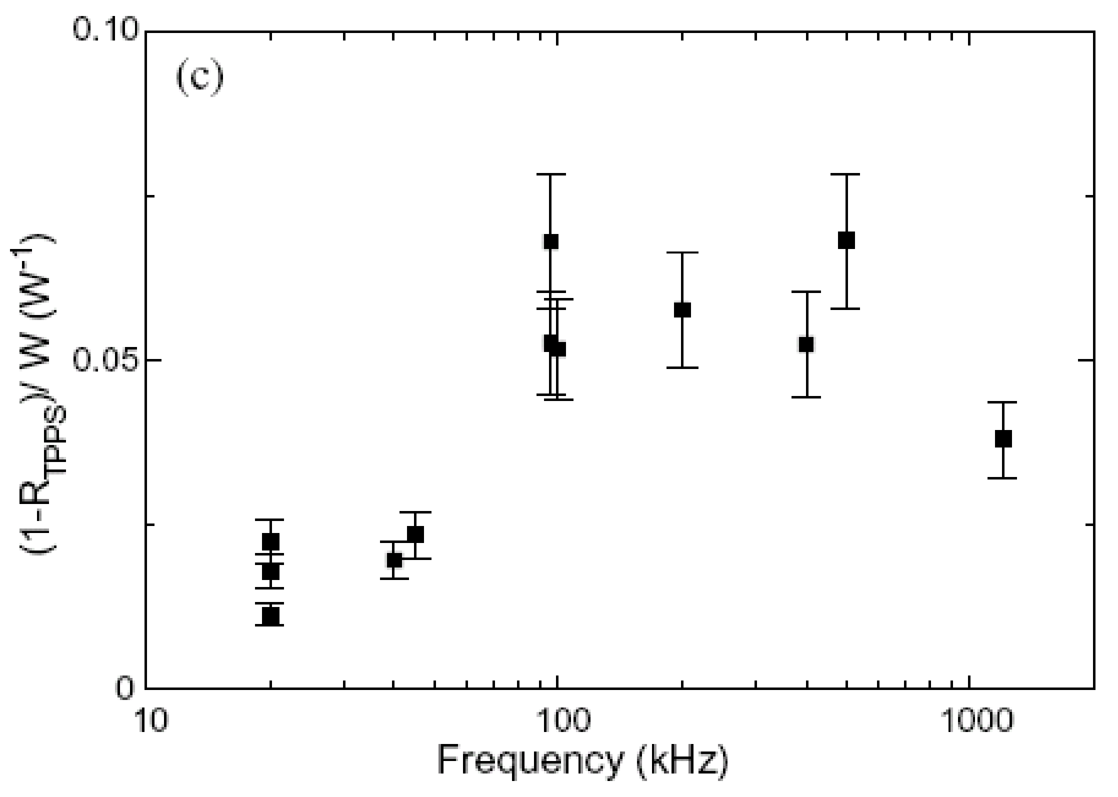
$$1 - R_{TPPS} = 1 - \frac{c_{TPPS}}{c_{TPPS}^{0}}$$



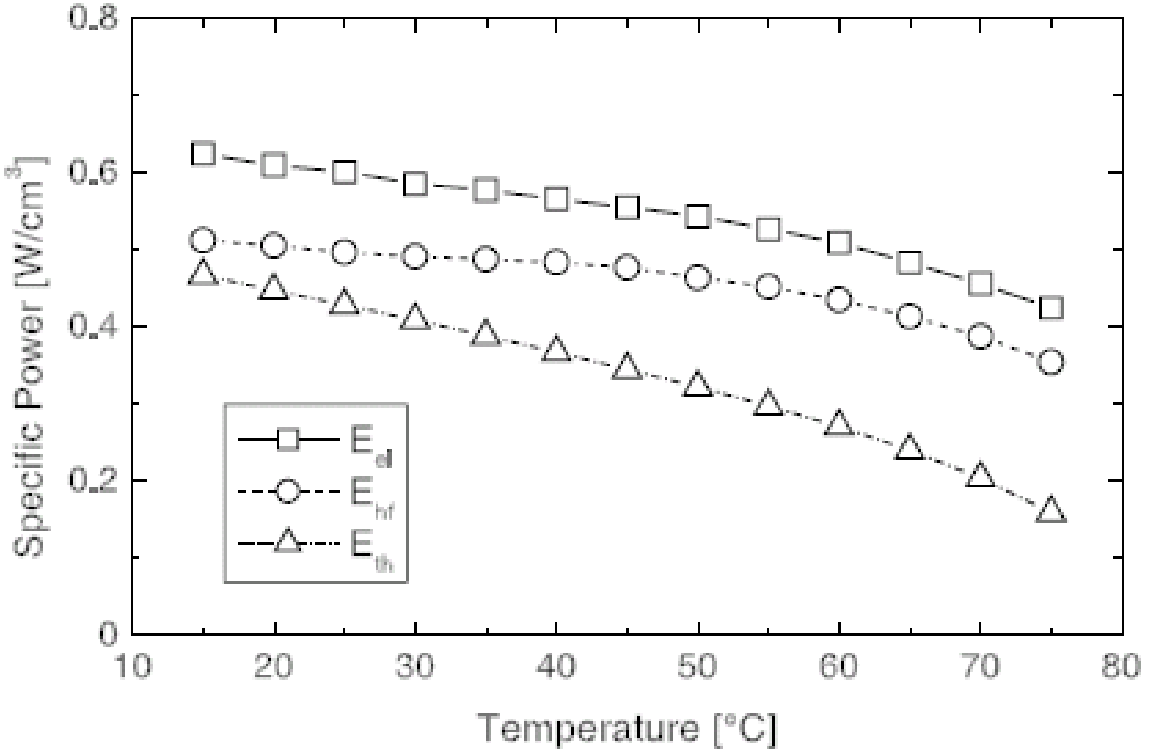
TPPS
3.3 10^{-6} M
Volume 50 cm^3

TPPS
$\lambda_{max} = 412$ nm
$\varepsilon = 500000\ dm^3\ mol^{-1}\ cm^{-1}$

Porphyrin Decomposition

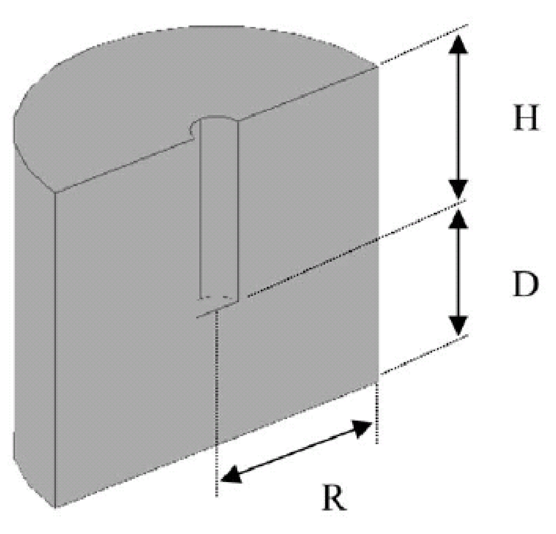


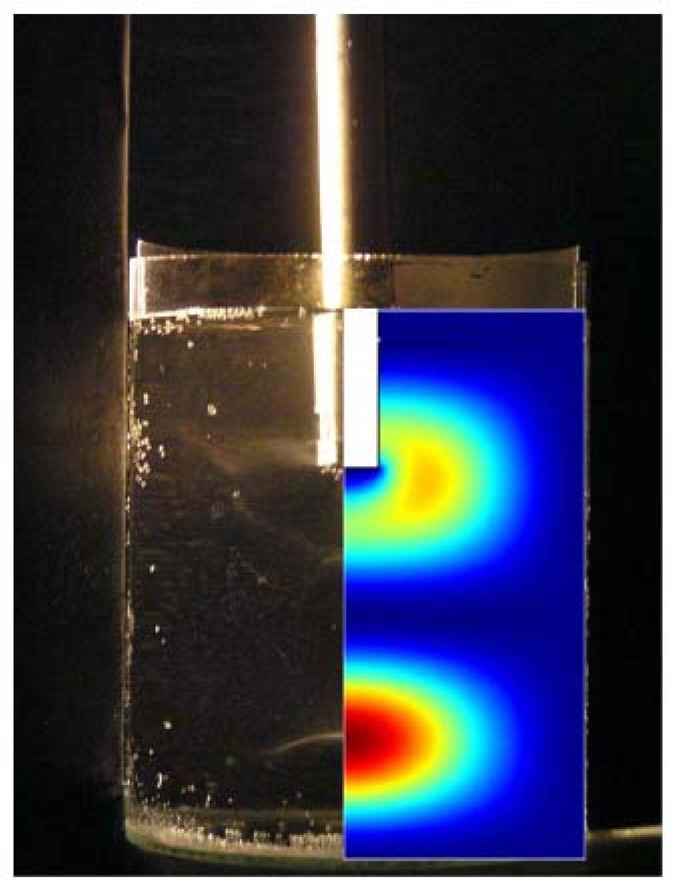
Power Measurement in Sonochemistry



Reactor Optimization

cavitating bubbles in the optimised cell (water, 20 kHz, P_{us} = 10 W) and simulated intensity distribution for the same geometry



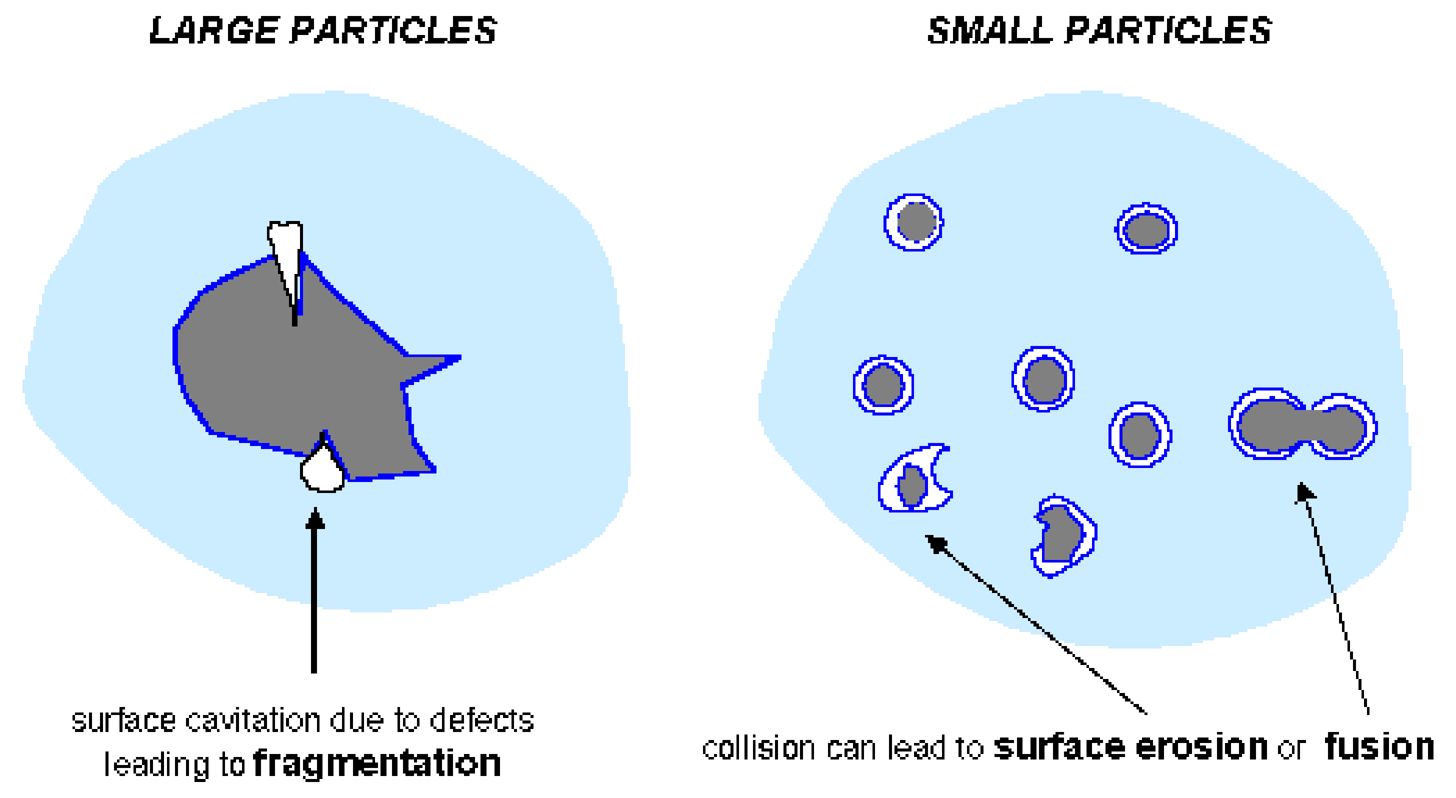


Heterogeneous Sonochemistry

Solid surfaces = implosion, microjets, shock waves
200 µm minimum particle size at 20 kHz for microjets

surface erosion
removal of unreactive coatings (oxides, nitrides, carbonaceous)
fragmentation of brittle materials, increased surface area

Heterogeneous Sonochemistry



LARGE PARTICLES

SMALL PARTICLES

surface cavitation due to defects
leading to **fragmentation**

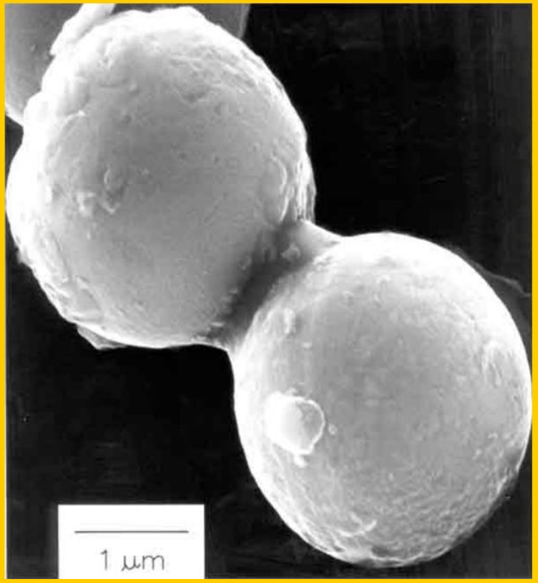
collision can lead to **surface erosion** or **fusion**

Heterogeneous Sonochemistry

Solid particles in liquid = shock waves

high speed interparticle collisions (500 km/s)

surface smoothing, surface coating removal
Ni catalytic activity in hydrogenation increased
10^5 fold by NiO removal



localized melting of metal particles at the impact
point fragmentation, increased surface area
intercalation rates enhanced 200 fold in layered
oxides and sulfides (V_2O_5, MoO_3, MoS_2, ZrS_2,
TaS_2)

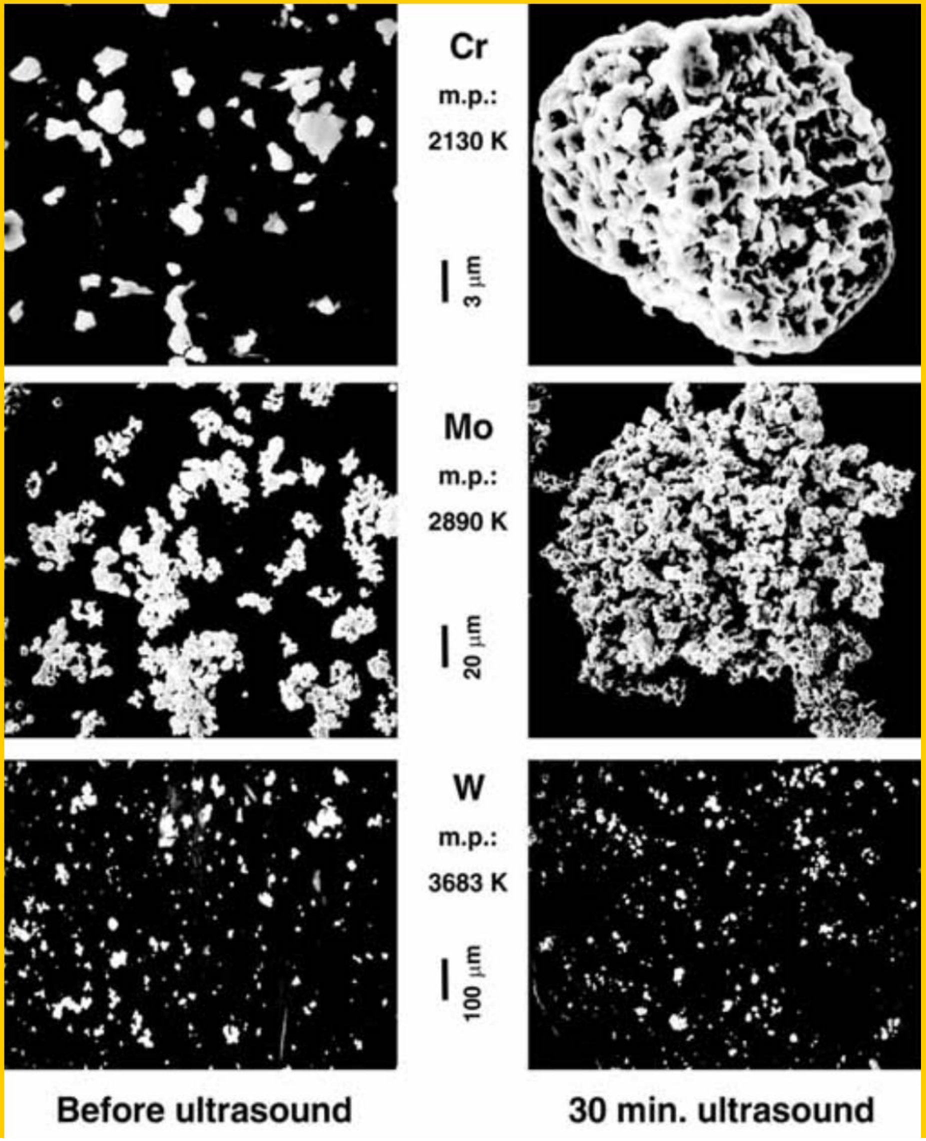
Heterogeneous Sonochemistry

Metal powders

Cr (mp 2130 K) and Mo (mp 2890 K) agglomerate

W (mp 3683 K) does not

temperature at the point of impact ~ 3000 °C



Cavitational Corrosion of the Tip

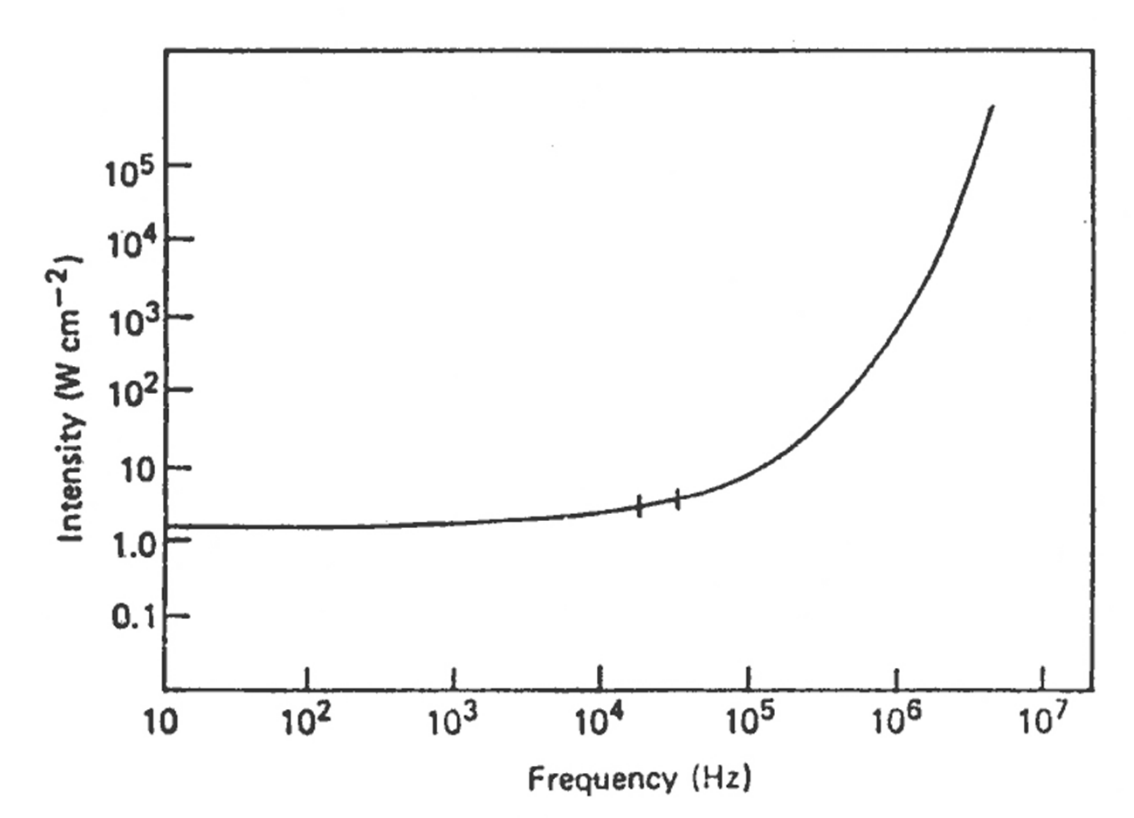
Control of Sonochemical Reactions

sound intensity - minimum for cavitation threshold, depends on frequency, optimum intensity for given reaction conditions, at high powers great number of bubbles hinder sound transmission, decoupling of a liquid from the source, breakdown of transducer material, 10 – 100 W cm^{-2}

sound frequency - 20 – 100 kHz, the higher the frequency, the higher power needed to actuate cavitation, stronger cavitation effects, rarefaction phase shortens at high frequency

sound attenuation - proportional to the frequency, more power needed at high frequencies

Effect of Frequency on Cavitation in Water



The frequency dependence of the intensity required to produce cavitation for degassed water at room temperature. The intensity required to produce vaporous cavitation above the frequency of 100 kHz rises rapidly.

Control of Sonochemical Reactions

volatile reactants - primary reaction site inside the bubbles, diameter 200 µm, 5000 °C, easy bubble formation, more reactant vapors inside bubbles, but the cavitation is cushioned

$Fe(CO)_5$ $Fe(acac)_3$ $FeSO_4$

nonvolatile reactants - reaction in the thin layer (200 nm) surrounding the bubble, 2000 °C, less cushioning, more energetic cavitation (collapse)

high boiling solvents - high vapor pressure inside the bubble cushions the implosion, nonvolatile solvents give less cushioning, more energetic cavitation
less cavitation in viscous liquids, viscosity resists shear forces
low surface tension facilitates cavitation, in water add surfactants

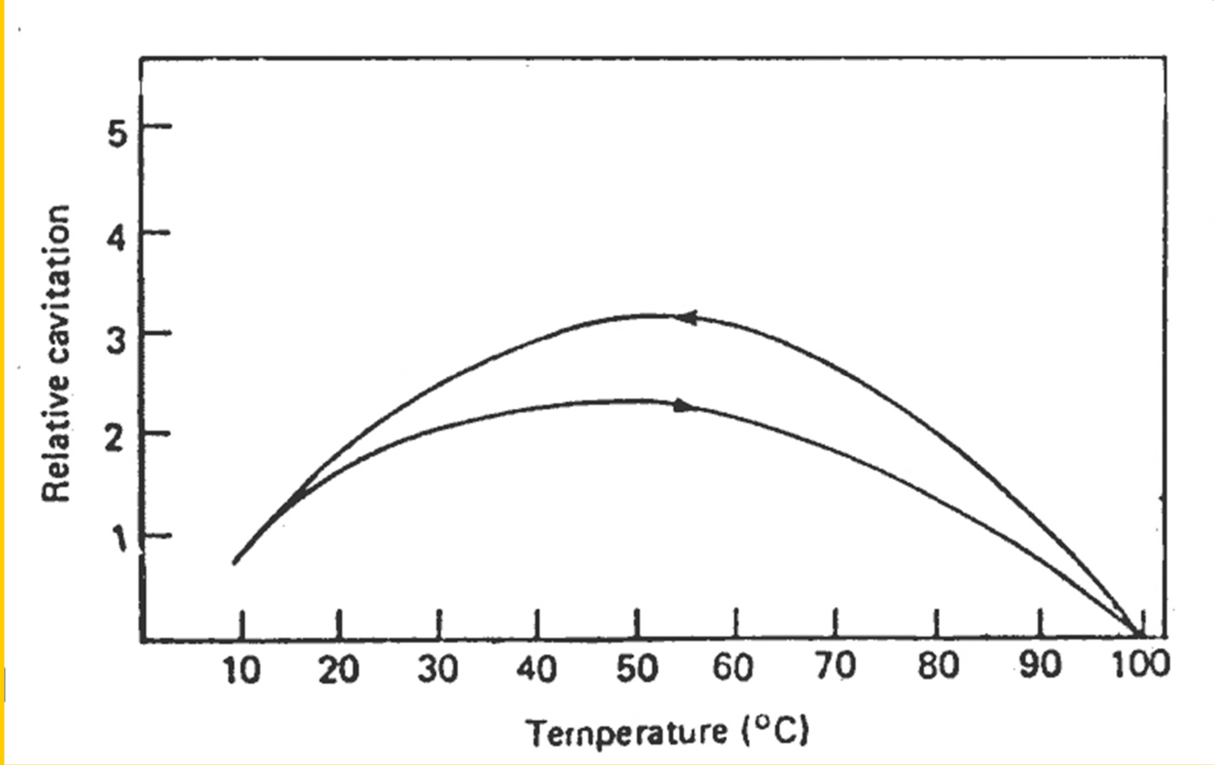
Control of Sonochemical Reactions

temperature - higher temperature increases vapor pressure of a medium, lowers viscosity and surface tension, many bubbles formed at temperatures close to solvent boiling point, a barrier to sound transmission, reaction rates decrease with increasing temperature, more vapors in bubbles

ambient gas
energy developed on bubble collapse:
monoatomic (Ar) > diatomic (N_2) > triatomic (CO_2)
Xe: low thermal conductivity, heat of the collapsing cavity retained
He: high thermal conductivity, heat of the collapsing cavity dissipitated, no reaction

external pressure - higher pressure suppresses bubble formation but makes cavitation more energetic, optimum pressure for a given frequency

Effect of Temperature on Cavitation in Water



The effect of temperature on cavitation and its associated hysteresis effect for tap water. The increase in intensity as the temperature is increased can be observed before it falls away at the boiling point. When the temperature is allowed to fall an increase in intensity is found in the region of 50-60 °C. This is quite a significant effect and appears to occur in all liquids.

Sonochemical Reactions

Solid surfaces = implosion, microjets, shock waves

200 µm minimum particle size at 20 kHz for microjets
surface erosion
removal of unreactive coatings (oxides, nitrides, carbonaceous)
fragmentation of brittle materials, increased surface area

Li, Mg, Zn, Al, Cu react at room temperature

$MCl_5 + Na + CO \rightarrow M(CO)_5^-$ **(M = V, Nb, Ta)**

$Mo + 6\,CO \rightarrow Mo(CO)_6$ **r. t., 1 bar,**
normally needs 300 bar, 300 °C

$R_2SiCl_2 + Li \rightarrow [\text{-}SiR_2\text{-}SiR_2\text{-}]_n + LiCl$
monomodal MW distribution

Homogeneous Sonochemical Reactions

Liquids = heating/cooling by cavity implosions

$H_2O \rightarrow H\cdot + OH\cdot \rightarrow H_2 + H_2O_2$

precursor decomposition:

metals $Fe(CO)_5 \rightarrow Fe + 5\,CO$

oxides $Ga^{3+} + H_2O \rightarrow$ Ga(O)(OH), diaspore

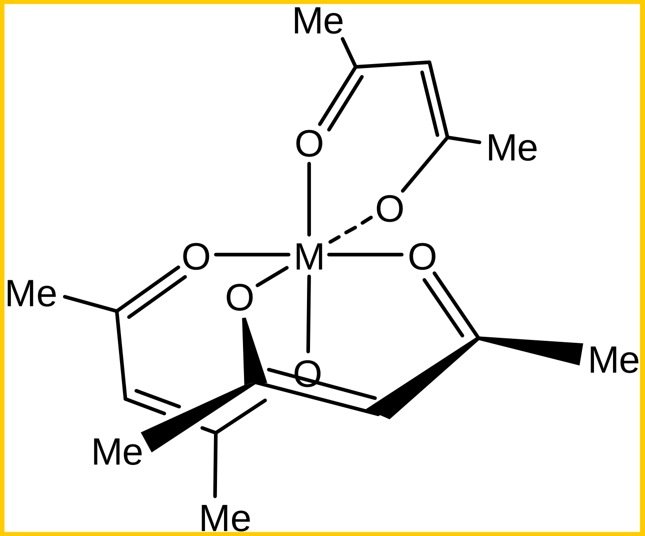
nitrides, carbides, sulfides

alkane cracking

polymer degradation, lower MW, surface modification

emulsification of immiscible liquids (oil-water, Hg-organics, polymer-inorganics)

$M(acac)_n$ as Precursors

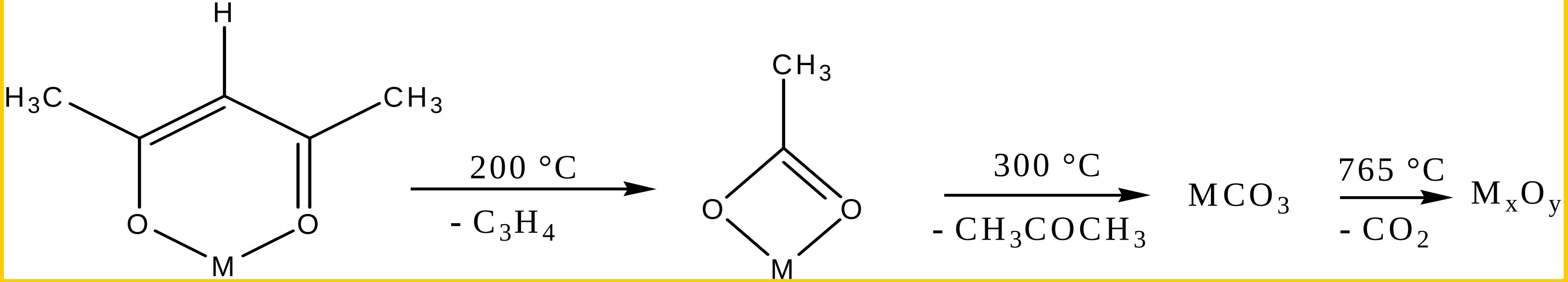


$M(acac)_3$

- Well studied class of compounds
- Many elements form acac complexes
- Metal complexes – precursors in CVD, sol-gel, thermolysis routes to oxides
- Easily chemically modified
- Volatile, organics soluble
- Nontoxic

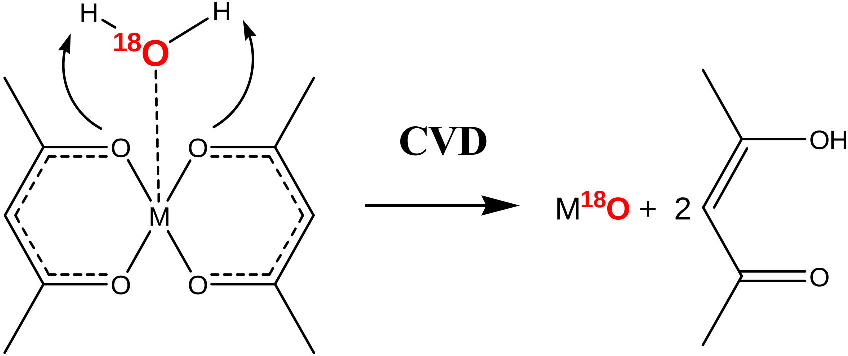
Chemistry of M(acac)$_n$ Precursors

Thermal decompositon pathway



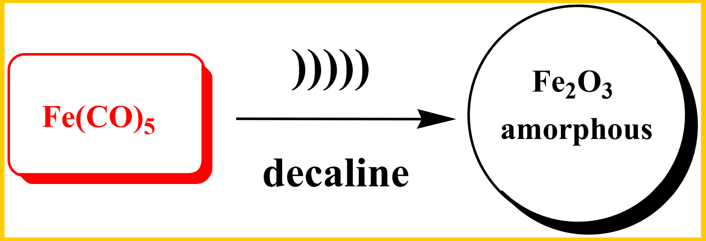
Ismail, H. M. *J. Anal. Appl. Pyrolysis* 1991, *21*, 315–326.

Ligand Removal by Water



Pinkas, J.; Huffman, J. C.; Baxter, D. V.; Chisholm, M. H.; Caulton, K. G. *Chem. Mater.* 1995, 7, 1589–1596.

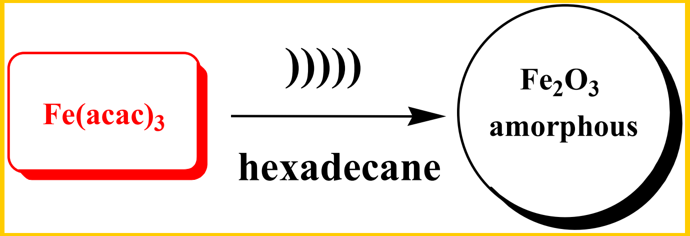
Sonochemical Synthesis of Iron Oxide Nanoparticles



$Fe(CO)_5 \xrightarrow[\text{decaline}]{)))))} Fe_2O_3$ amorphous

Cao, X.; Prozorov, R.; Koltypin, Y.; Kataby, G.; Felner, I.; Gedanken, A. *J. Mater. Res.* 1997, 12, 402–406.

Cao, X.; Koltypin, Yu.; Prozorov, R.; Katabya, G.; Gedanken, A. *J. Mater. Chem.* 1997, 7, 2447–2451.

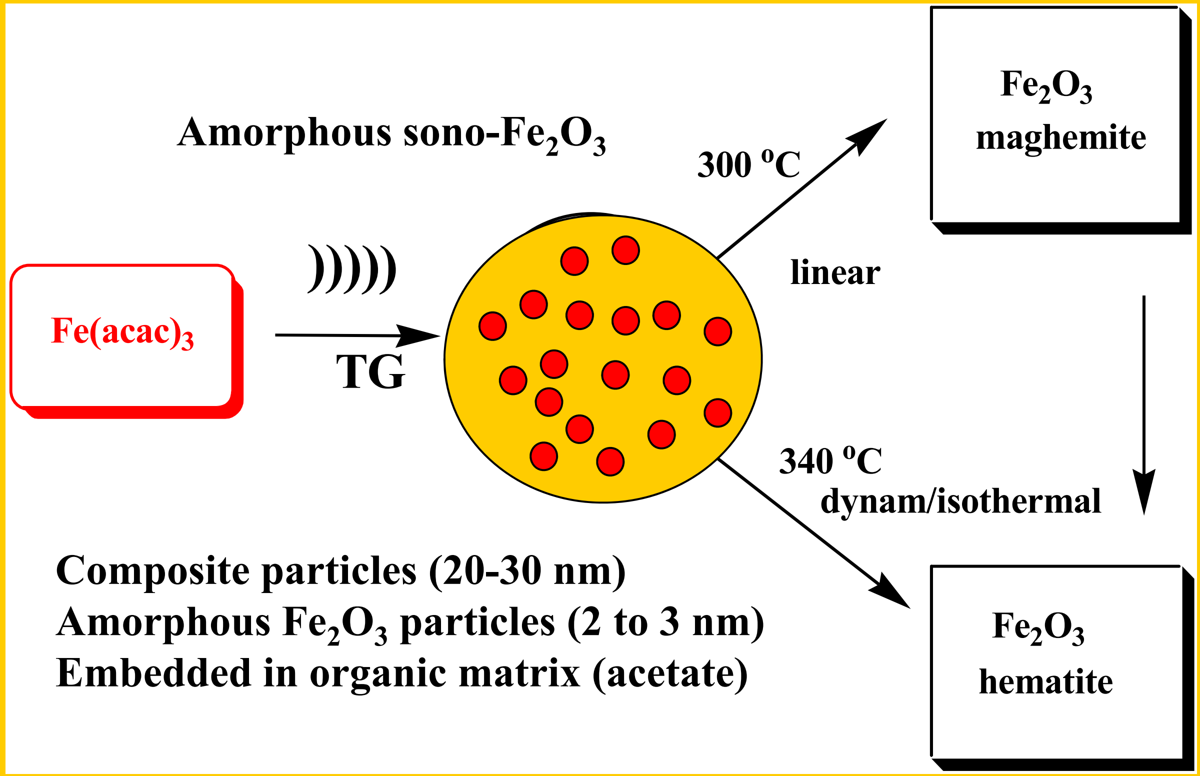


$Fe(acac)_3 \xrightarrow[\text{hexadecane}]{)))))} Fe_2O_3$ amorphous

Amorphous product, by heating to 700 ºC converted to α-Fe_2O_3 20–40 nm

Nikitenko, S. I.; Moisy, Ph.; Seliverstov, A. F.; Blanc, P.; Madic, C. *Ultrasonics Sonochem.* 2003, 10, 95–102.

Sonochemical Synthesis of Iron Oxide Nanoparticles



$Fe(acac)_3$

)))))

TG

Amorphous sono-Fe_2O_3

300 °C

linear

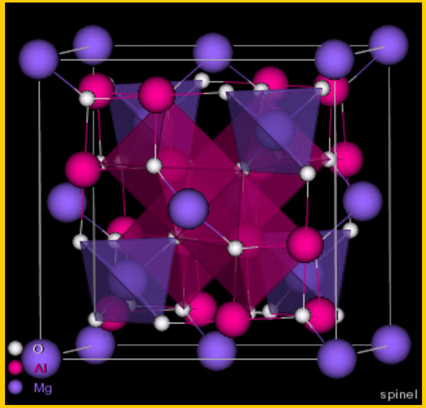
340 °C
dynam/isothermal

Fe_2O_3
maghemite

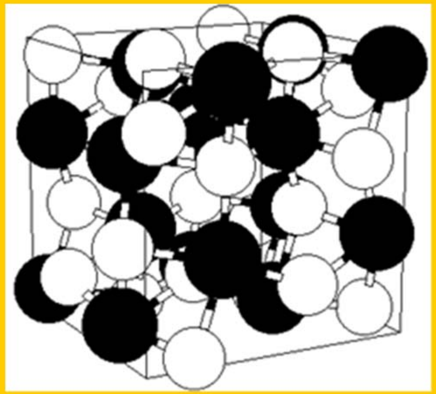
Fe_2O_3
hematite

Composite particles (20-30 nm)
Amorphous Fe_2O_3 particles (2 to 3 nm)
Embedded in organic matrix (acetate)

Defect spinel



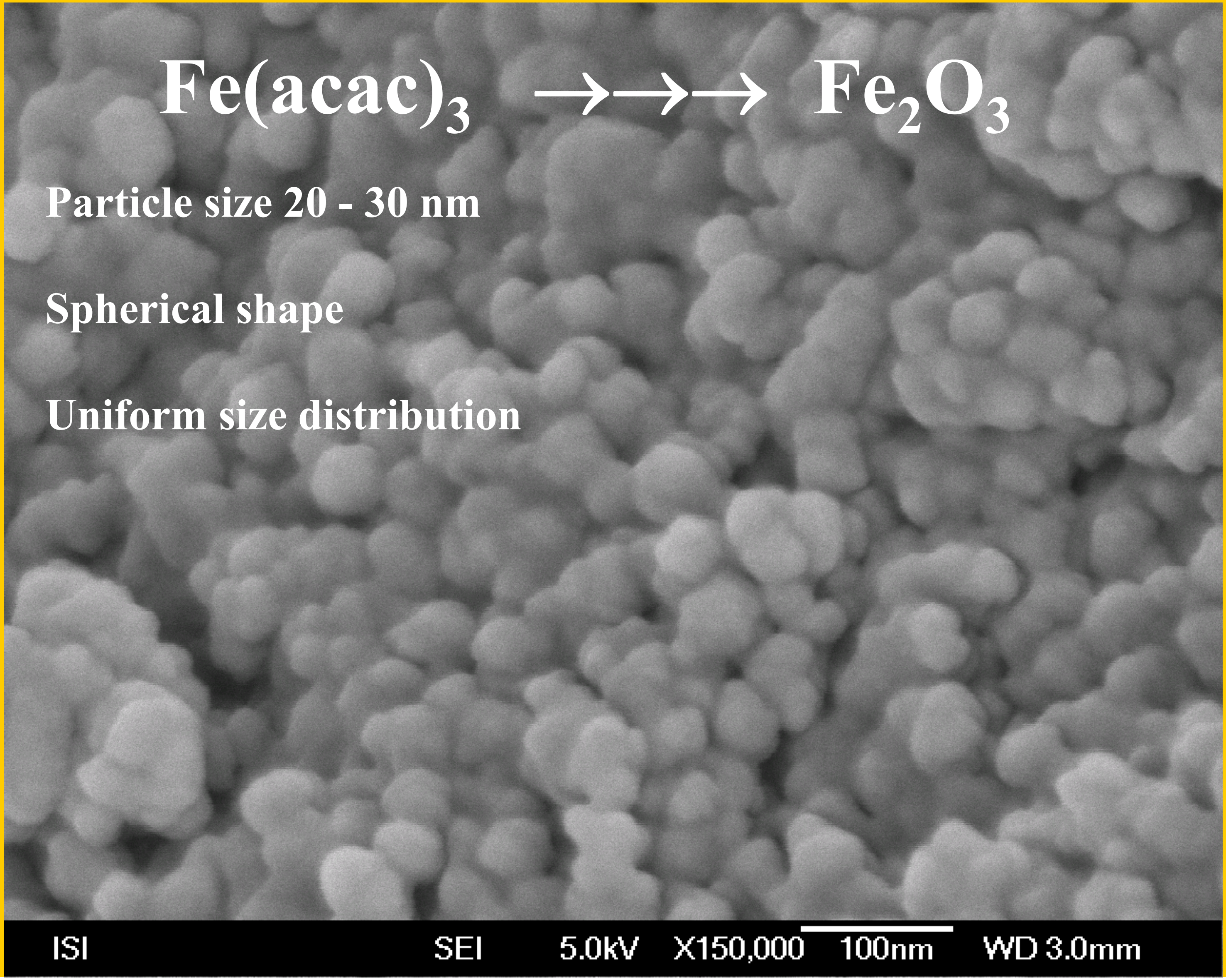
Corundum



J. Pinkas, V. Reichlova, R. Zboril, Z. Moravec, P. Bezdicka, J. Matejkova: Sonochemical synthesis of amorphous nanoscopic iron(III) oxide from $Fe(acac)_3$

Ultrasonic Sonochem. 2008, *15*, 256-264

SEM of Nanoscopic Fe_2O_3



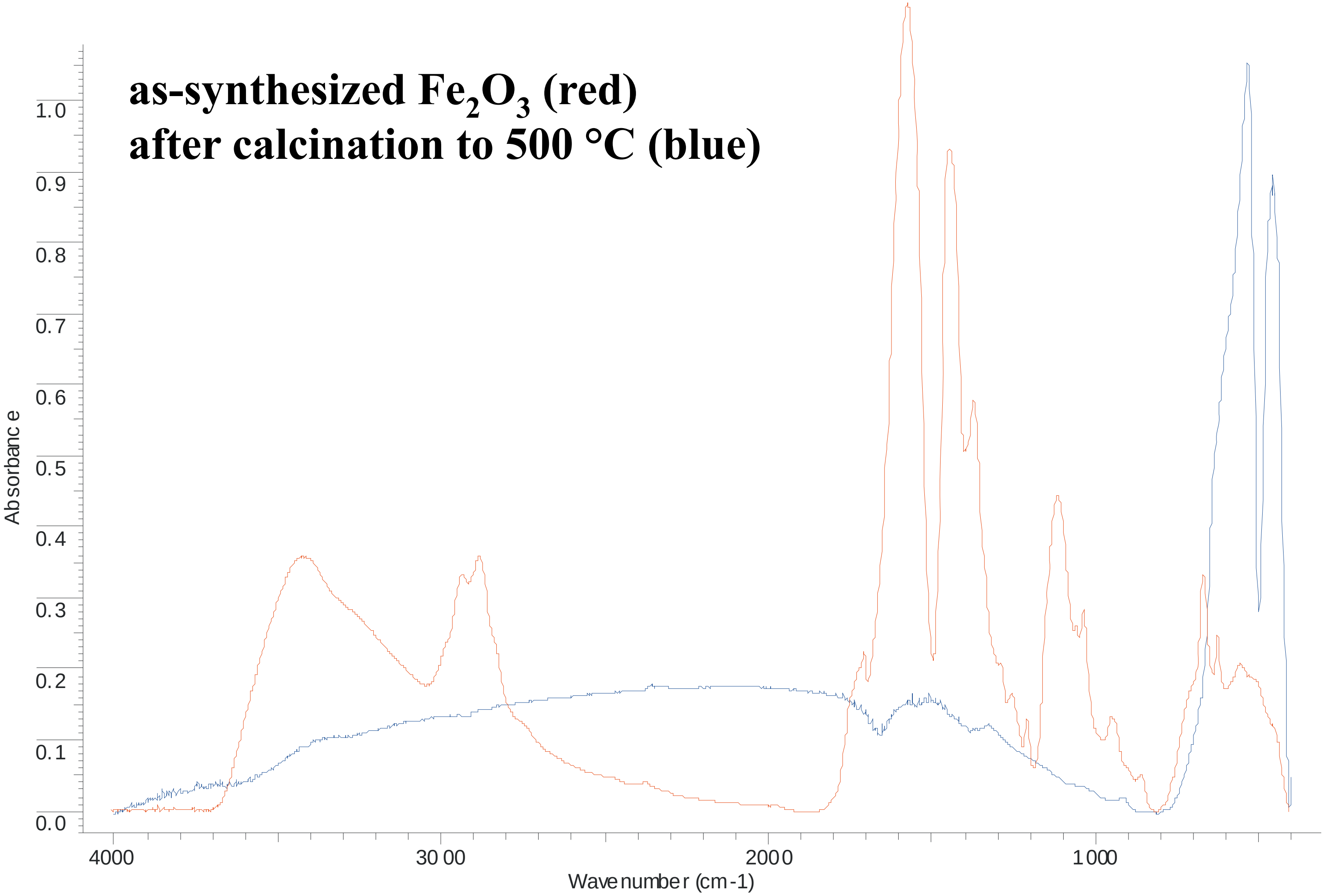
$Fe(acac)_3 \rightarrow\rightarrow\rightarrow Fe_2O_3$

Particle size 20 - 30 nm

Spherical shape

Uniform size distribution

IR Spectrum of Sono-Fe_2O_3

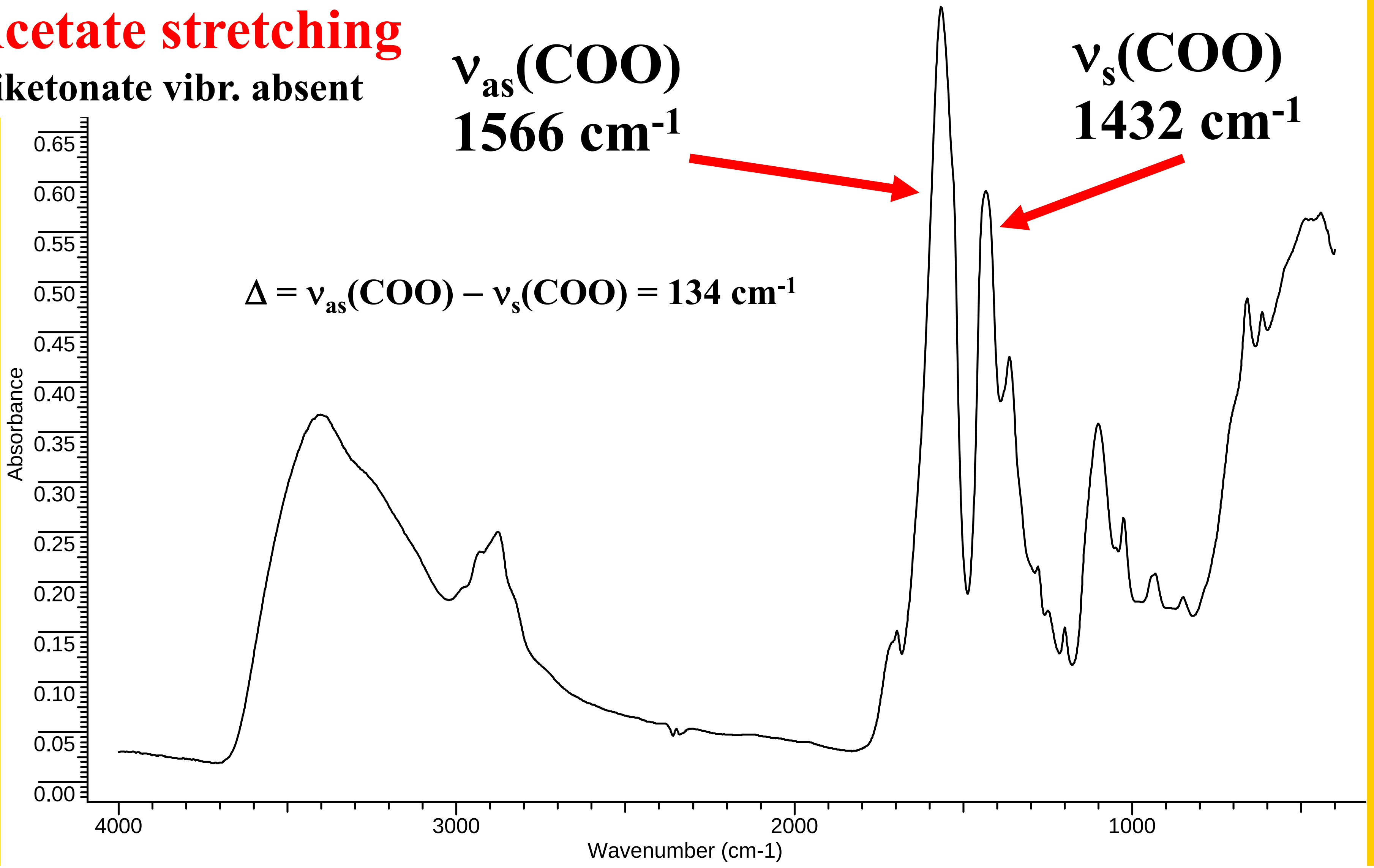


as-synthesized Fe_2O_3 (red)
after calcination to 500 °C (blue)

IR Spectrum of Sono-Fe_2O_3

Acetate stretching

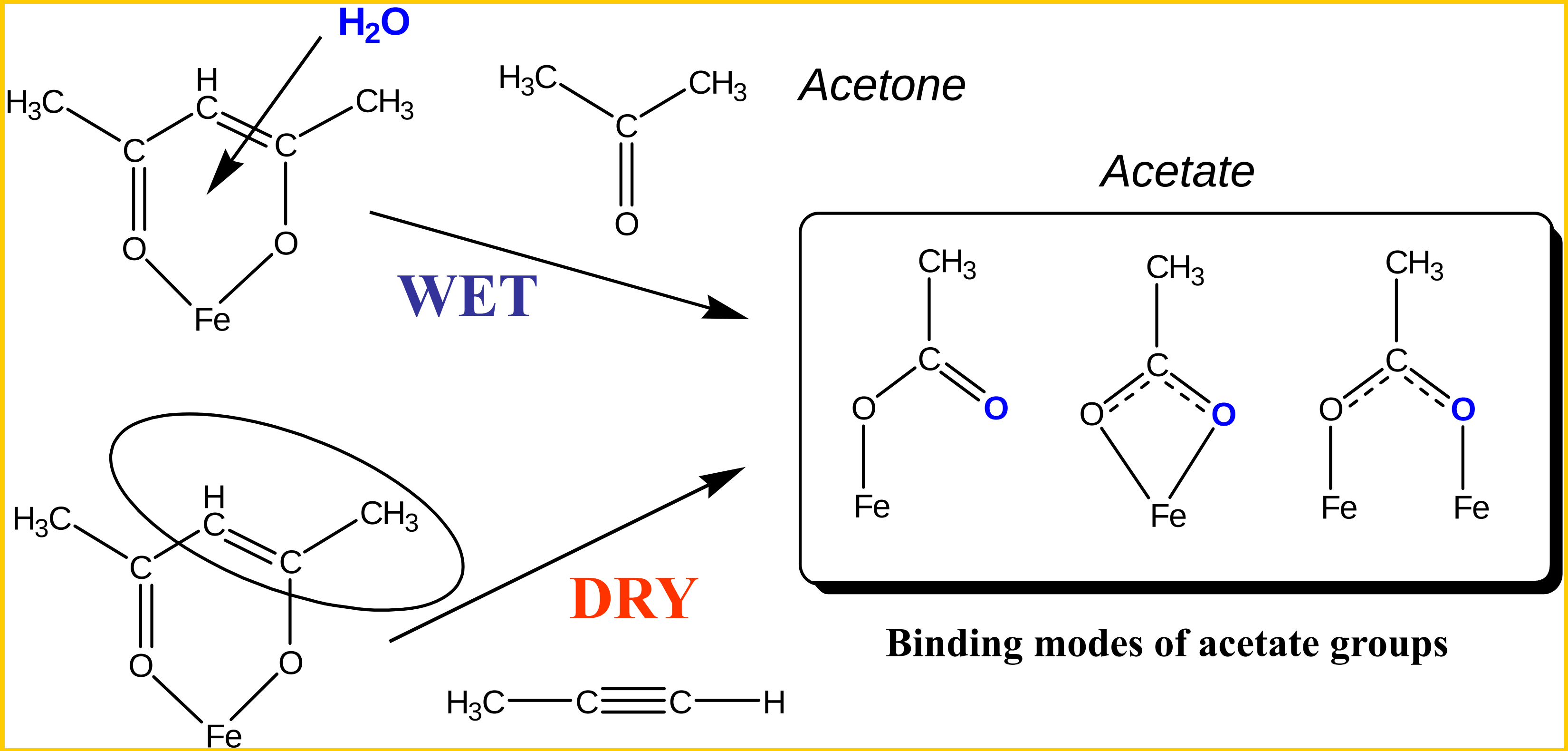
Diketonate vibr. absent



$\Delta = \nu_{as}(COO) - \nu_s(COO) = 134\ cm^{-1}$

Decomposition of Acac Ligands

Speculation about the nature of residual organic groups



Binding modes of acetate groups

Deacon-Phillips Rules

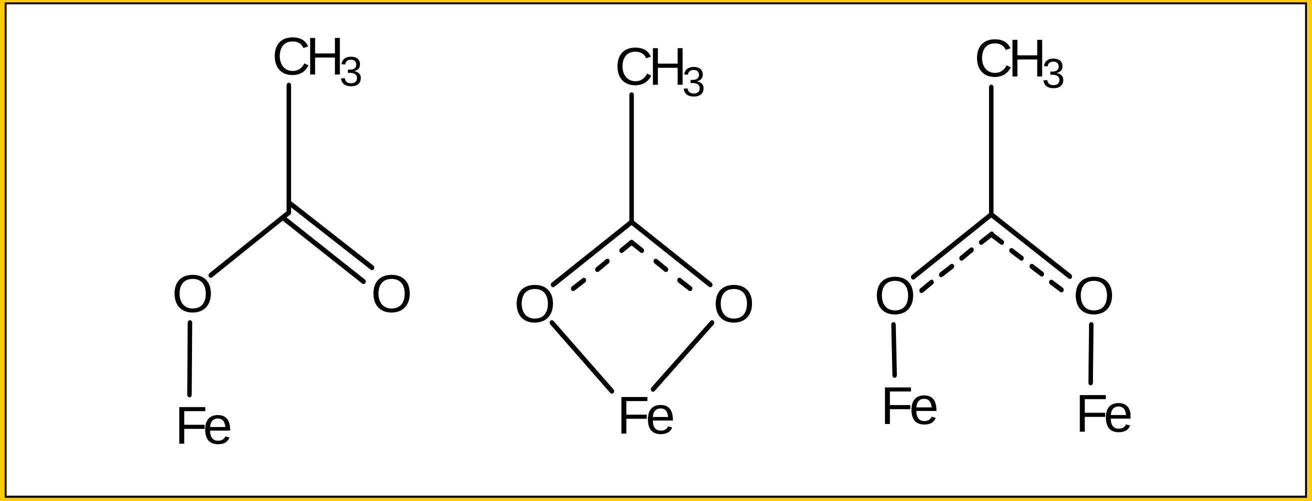
$\Delta = \nu_{as}(COO) - \nu_{s}(COO)$

$\Delta\ CH_3COO^{-} = 164\ cm^{-1}$

Δ larger than ionic form = unidentate

Δ smaller than ionic form = bidentate

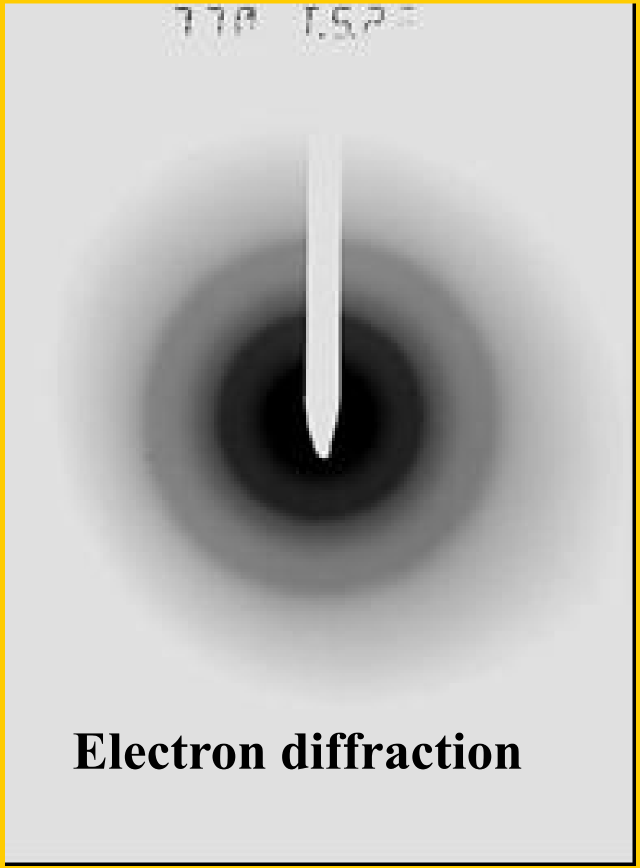
Δ comparable to ionic form = bridging

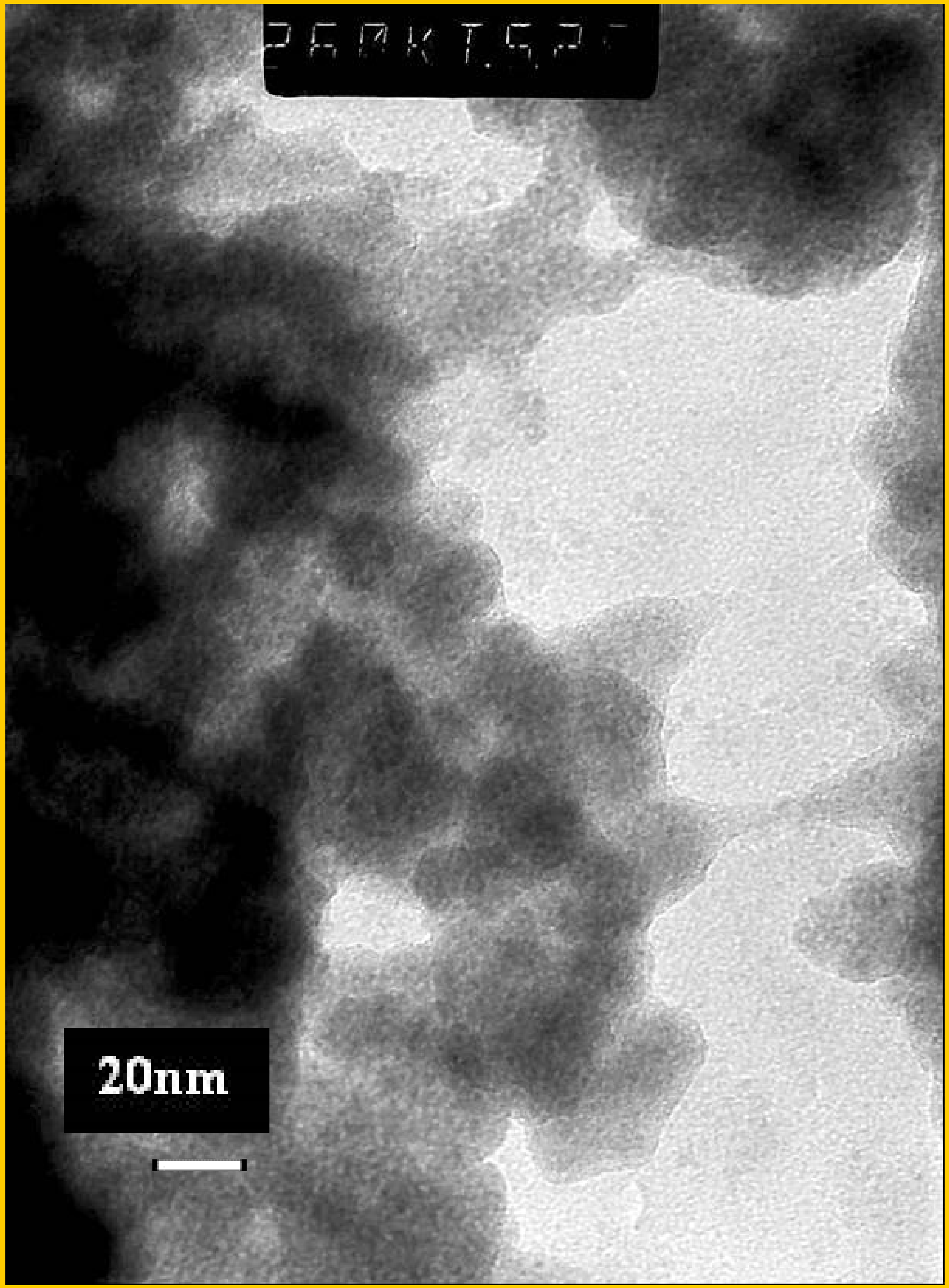


Deacon, G. B.; Phillips, R. J. *Coord. Chem. Rev.* 1980, 3, 227–250.

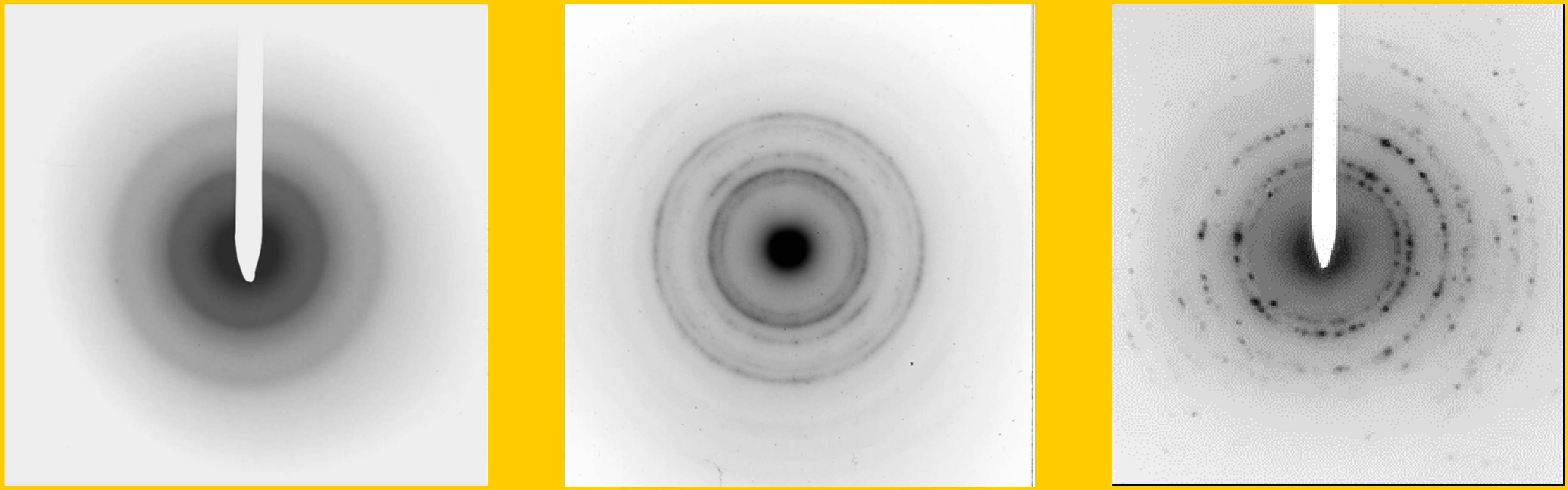
TEM

proves amorphous character of sono-Fe_2O_3


Electron diffraction



Crystallization of Amorphous Fe_2O_3 under TEM Beam

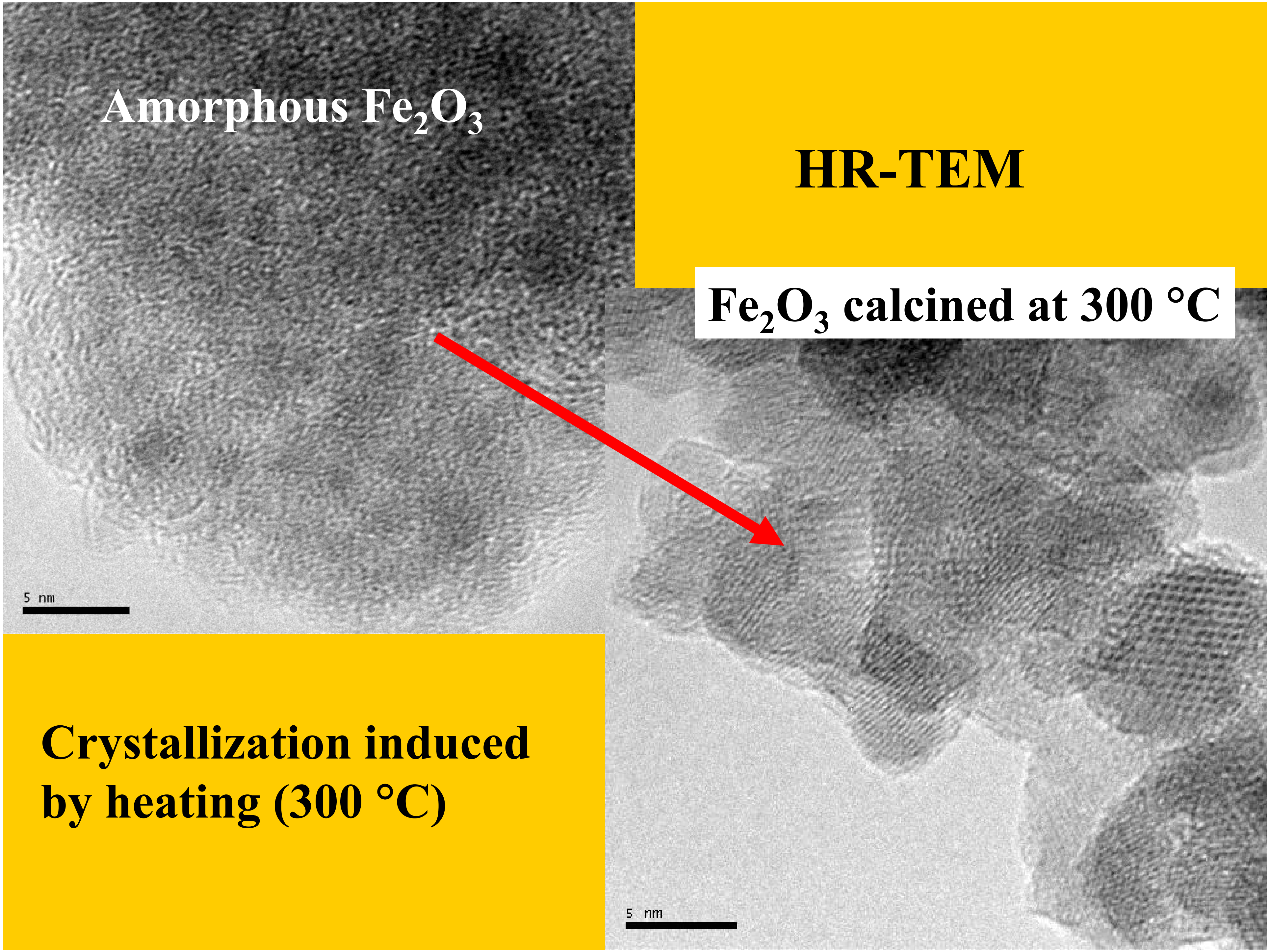


Electron diffraction

Maghemite or Magnetite

Time under TEM beam

HR-TEM

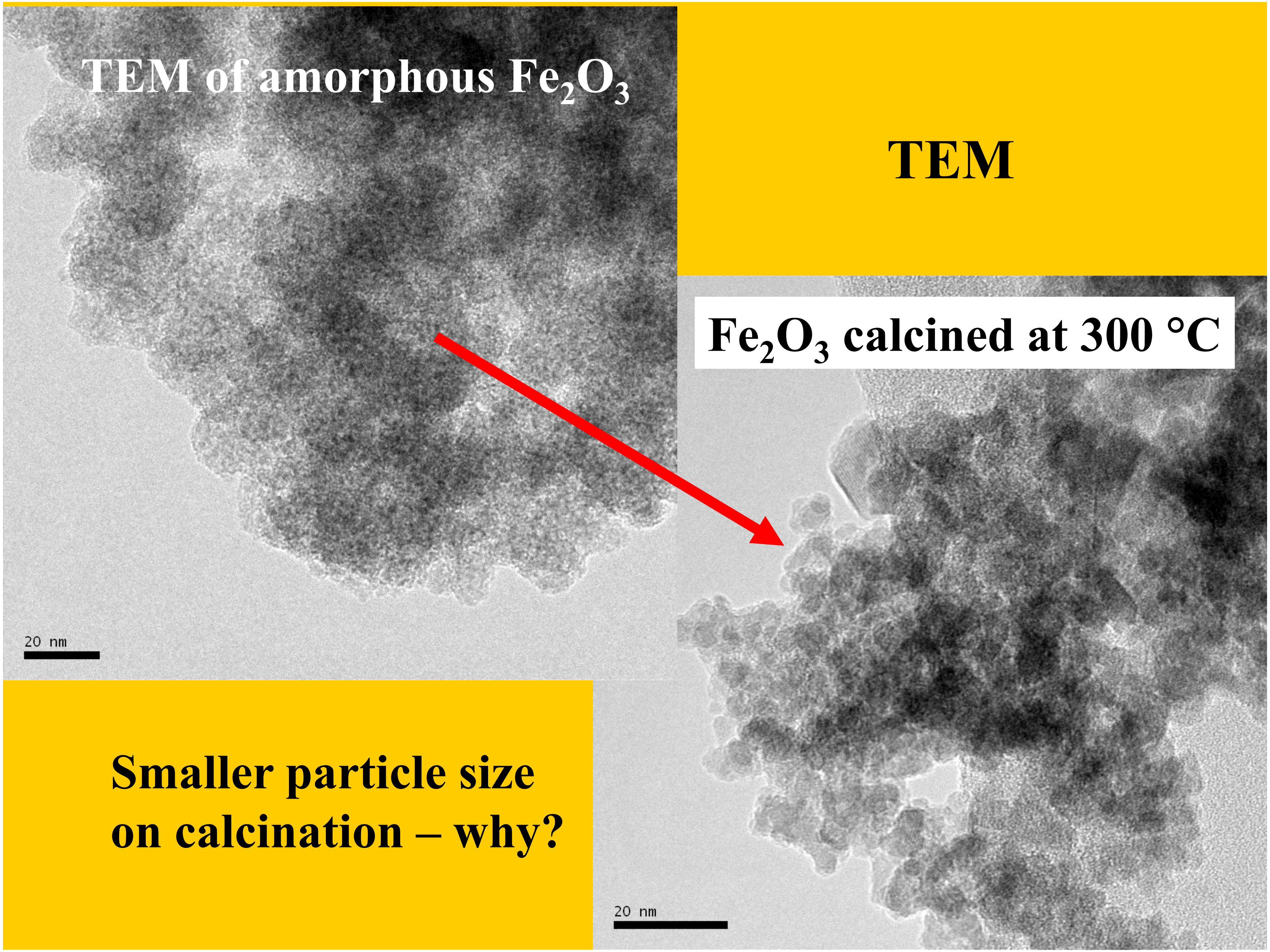


Amorphous Fe_2O_3

Fe_2O_3 calcined at 300 °C

Crystallization induced by heating (300 °C)

TEM



TEM of amorphous Fe_2O_3

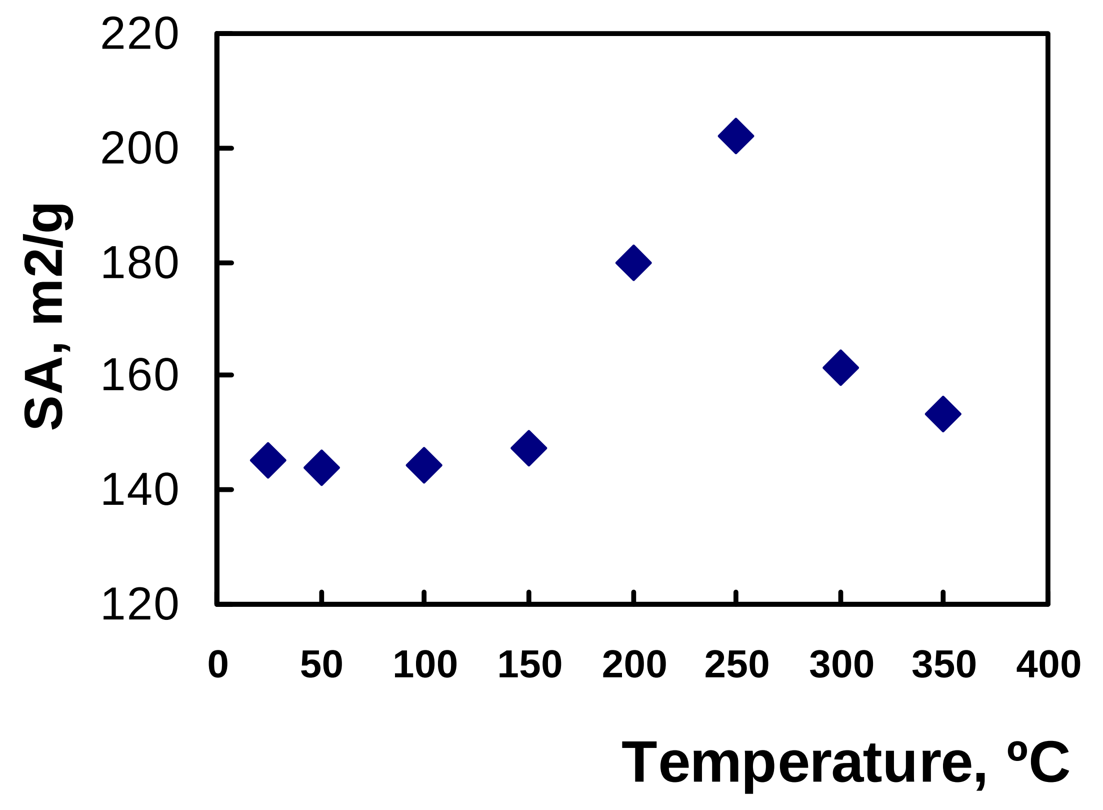
Fe_2O_3 calcined at 300 °C

Smaller particle size on calcination – why?

Specific Surface Area

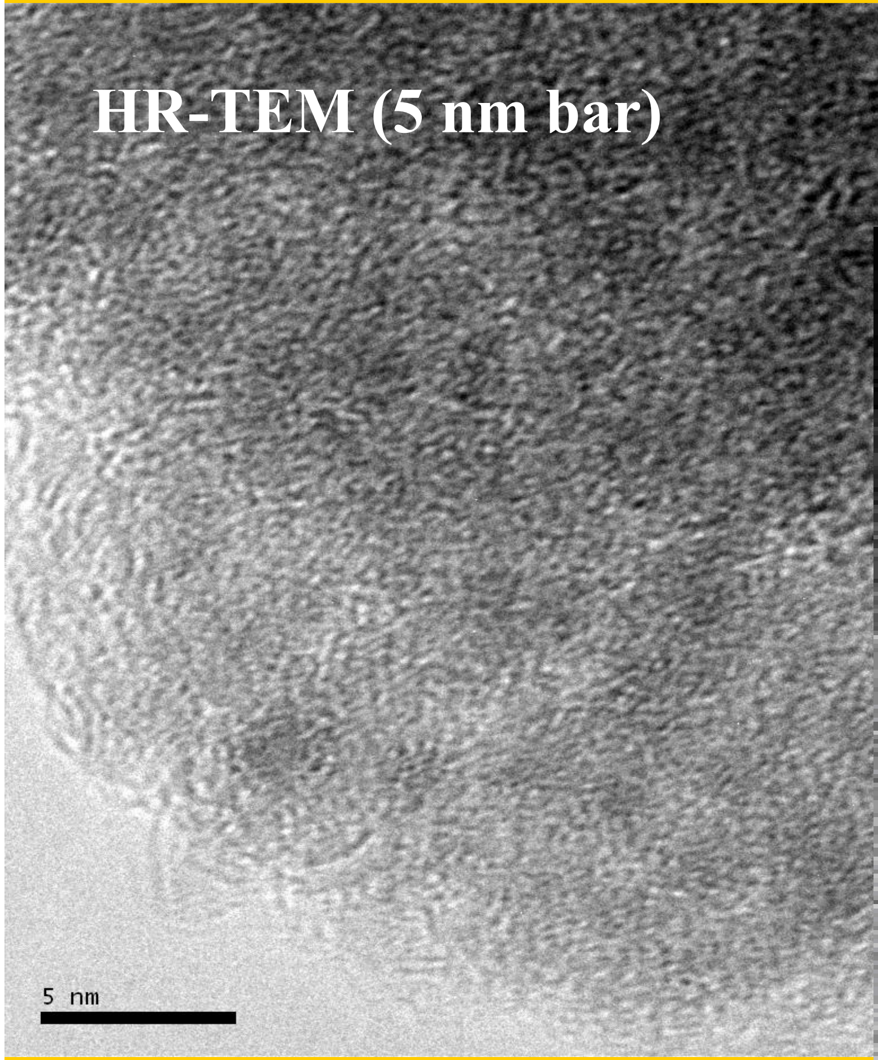
Surface area 48 to 260 m^2 g^{-1} (BET) depending on **H_2O content**

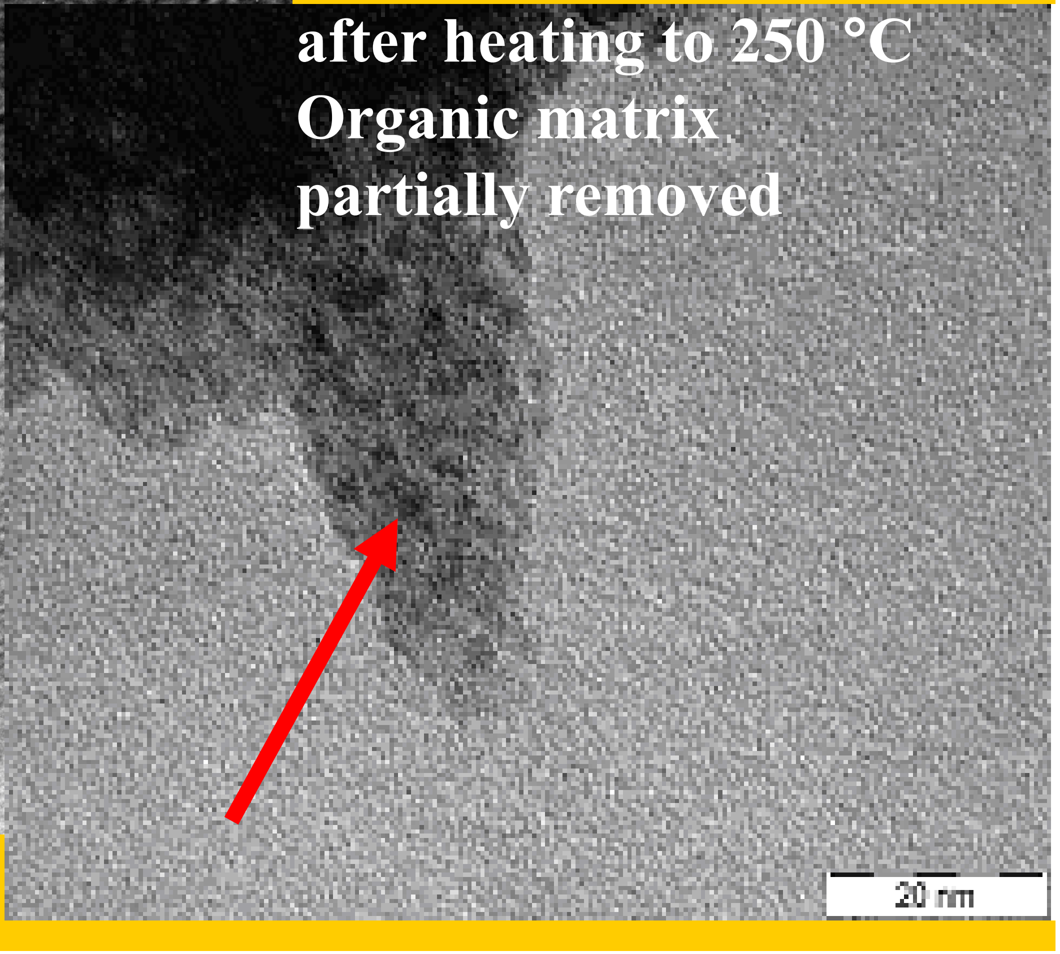
BET surface area of the Fe_2O_3 heated to different temperatures during 12h outgassing periods



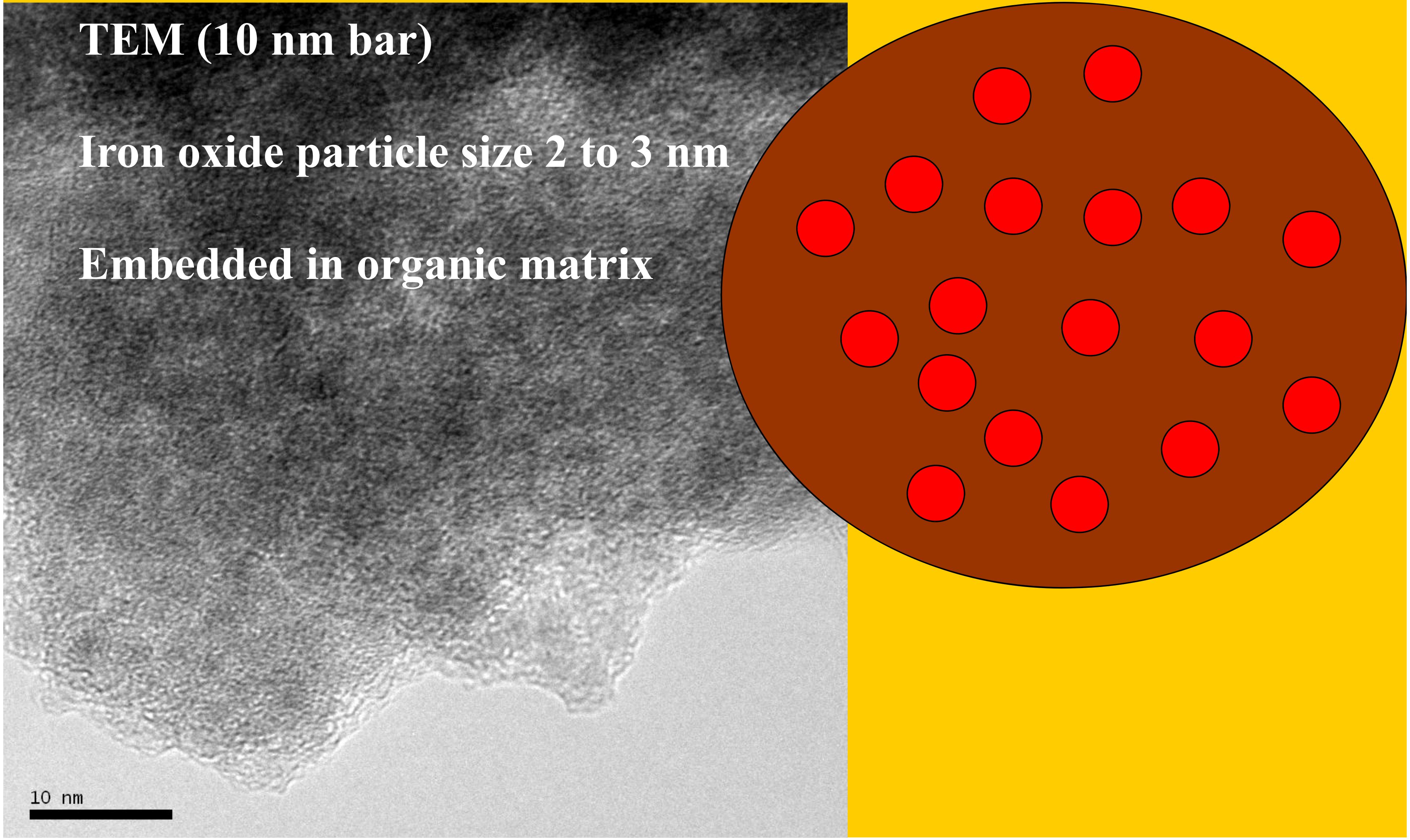
The oxide surface area increases as the acetate groups are removed, then the particle size increases because of sintering

Composite Particles of Sono-Fe_2O_3


HR-TEM (5 nm bar)


TEM (20 nm bar)
after heating to 250 °C
Organic matrix
partially removed

Composite Particles of Fe_2O_3



TEM (10 nm bar)

Iron oxide particle size 2 to 3 nm

Embedded in organic matrix

XRD

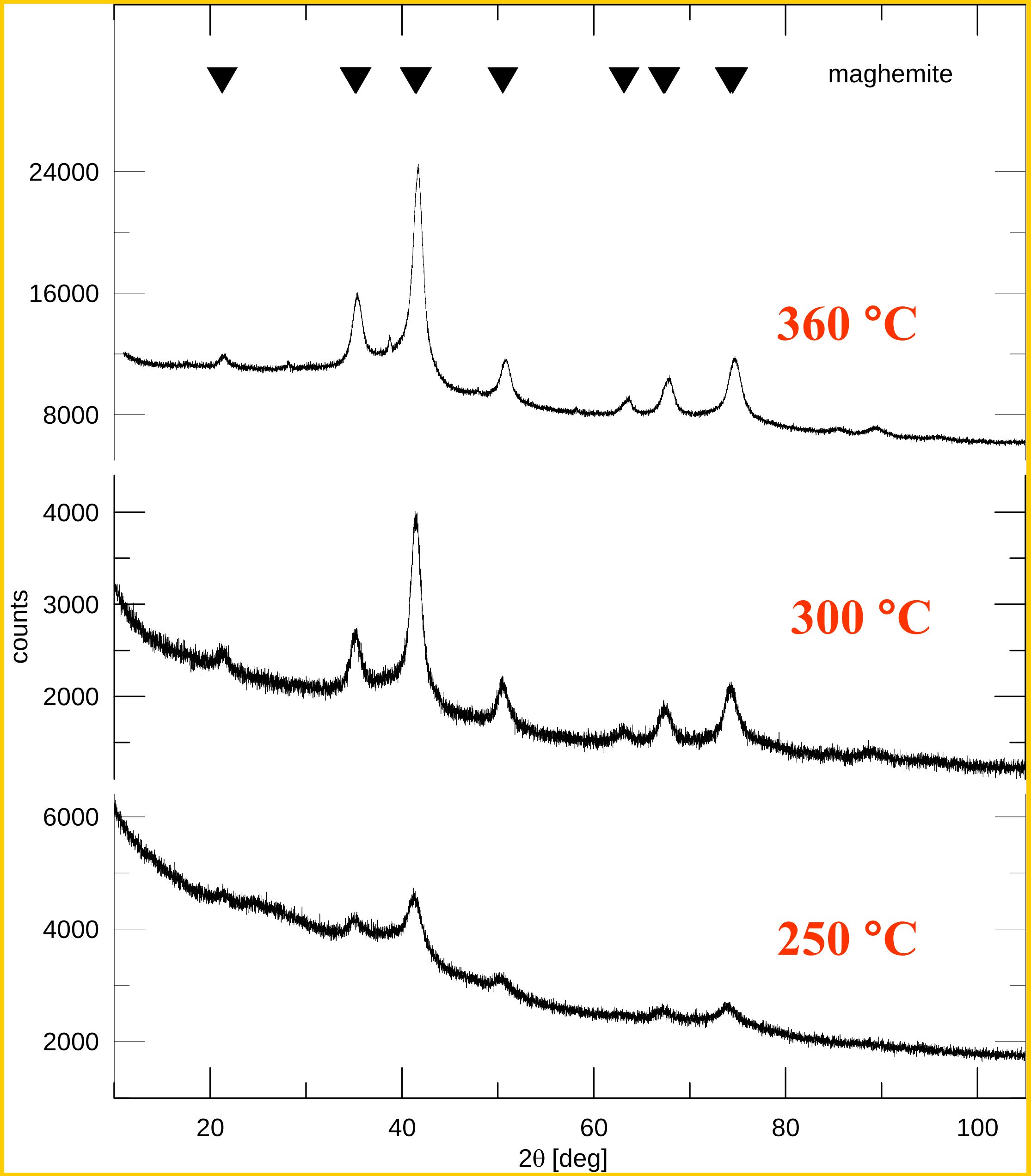
of amorphous Fe_2O_3

heated dynamically in air

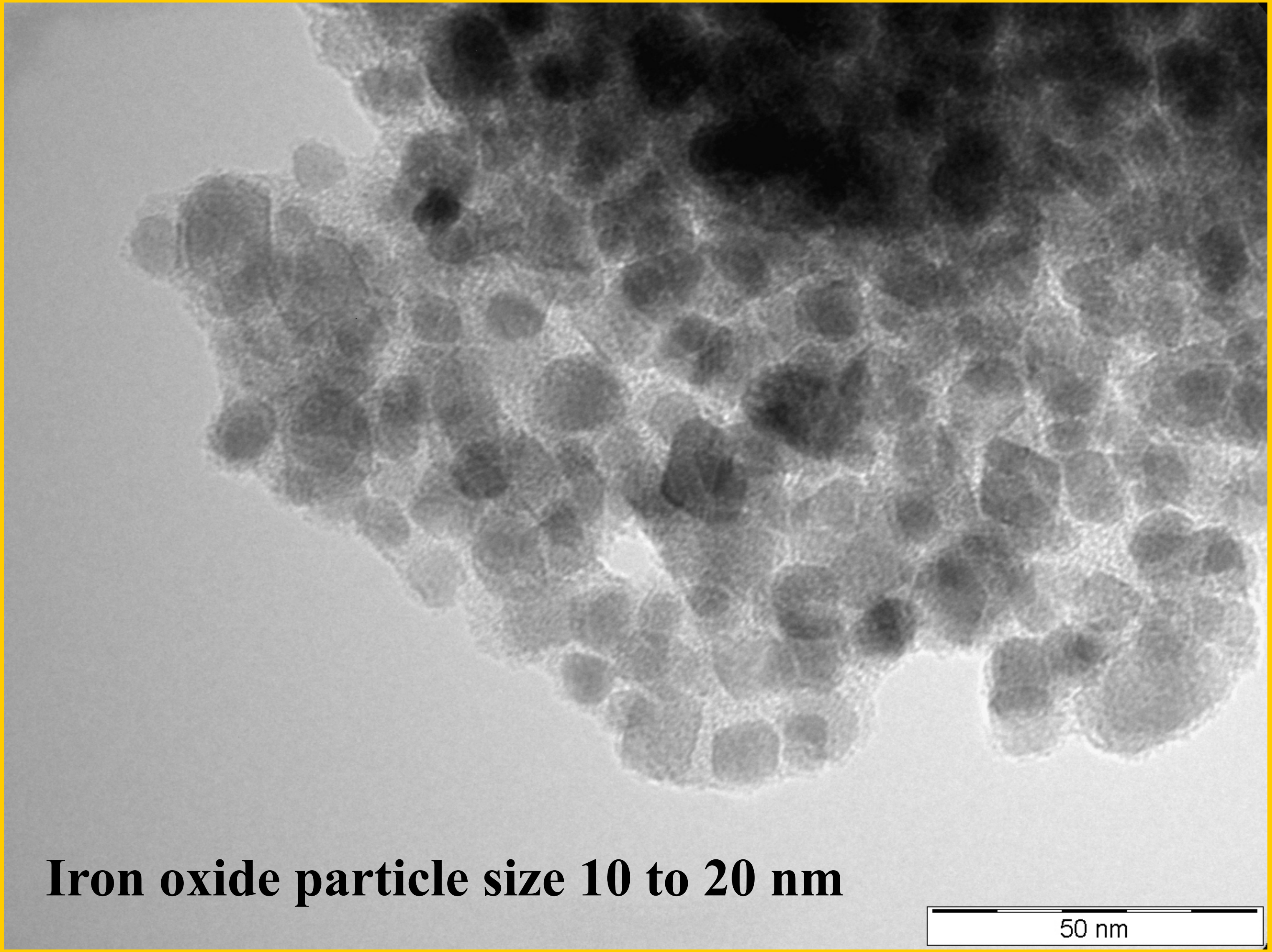
up to 250, 300, and 360 °C

Maghemite

γ - Fe_2O_3

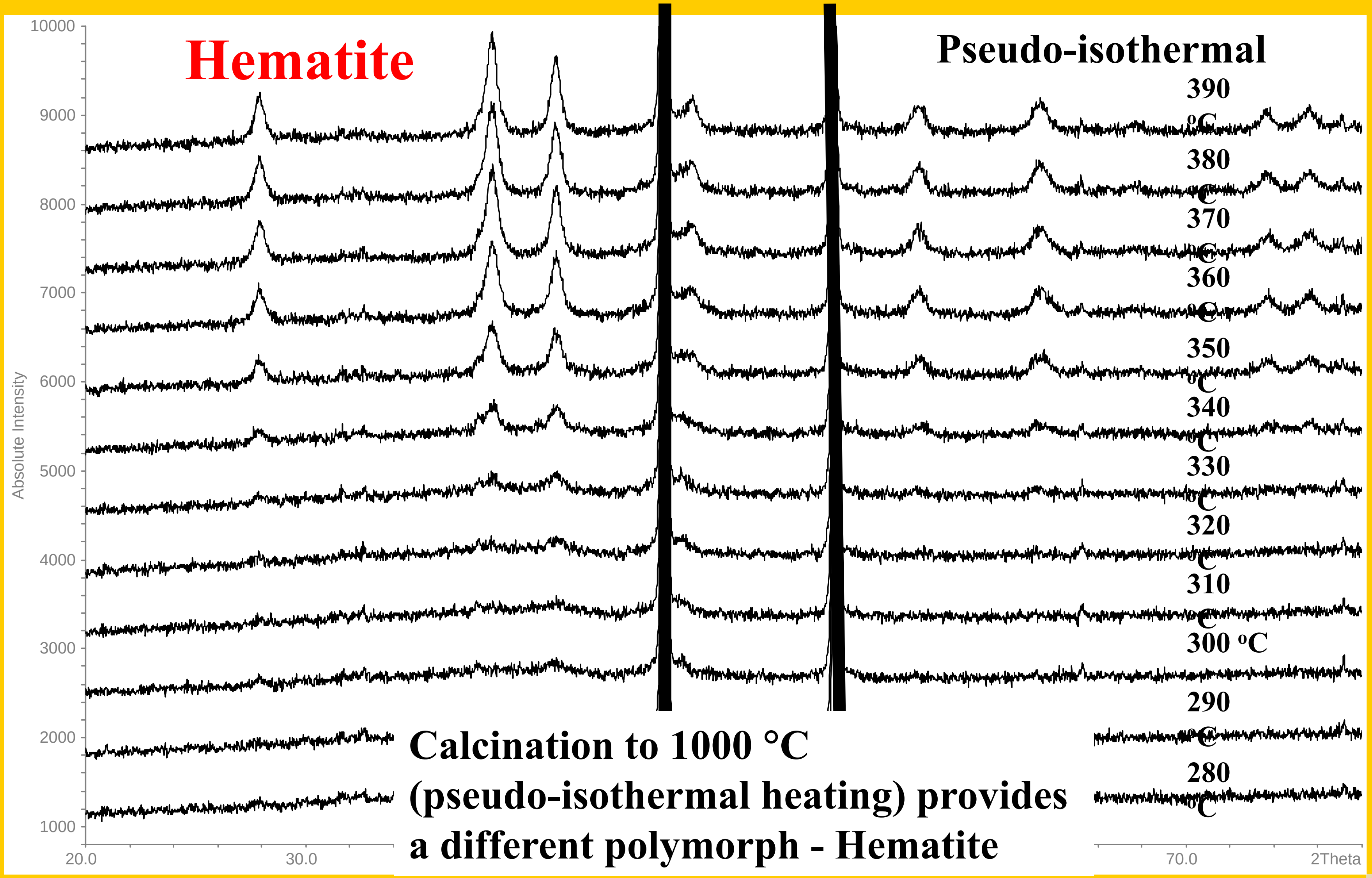


TEM of Fe_2O_3 Calcined at 600 °C



Iron oxide particle size 10 to 20 nm

HT-XRD of Sono-Fe_2O_3 280 - 390 °C

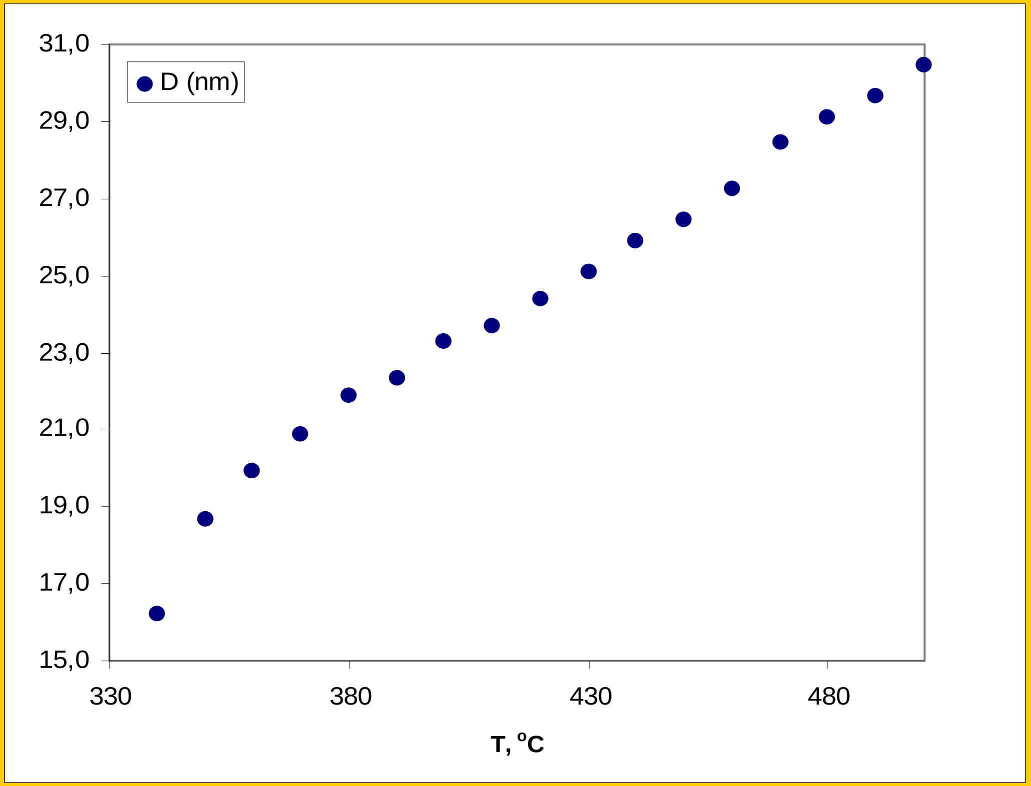


Calcination to 1000 °C (pseudo-isothermal heating) provides a different polymorph - Hematite

Ramp 1 °C min^{-1}, 1 min equilb., 30 min data collect., 10 °C steps

Hematite Particle Size

coherence length D (nm)



Dependence of the coherence length, D (nm) of α-Fe_2O_3 on the crystallization temperature under dynamic-isothermal conditions of the HT-XRD measurement