

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

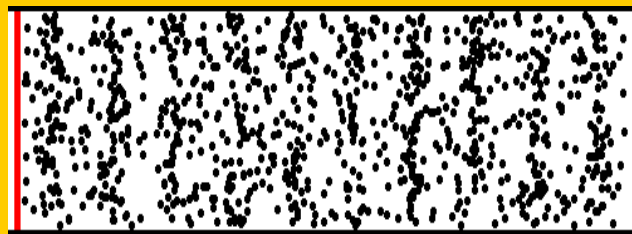
Sound = pressure waves = periodic compression/expansion cycles traveling through a medium possessing elastic properties (gas, liquid, solid)

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

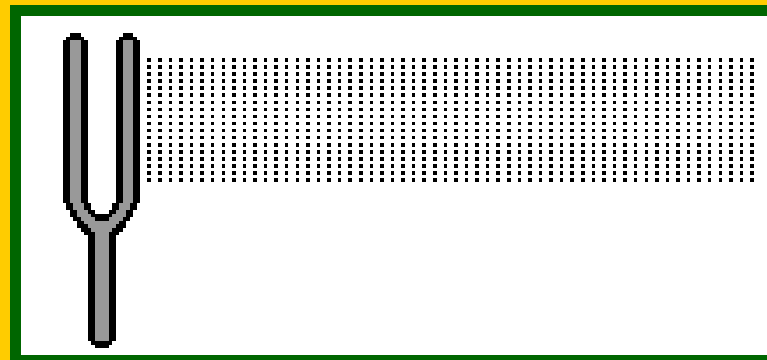
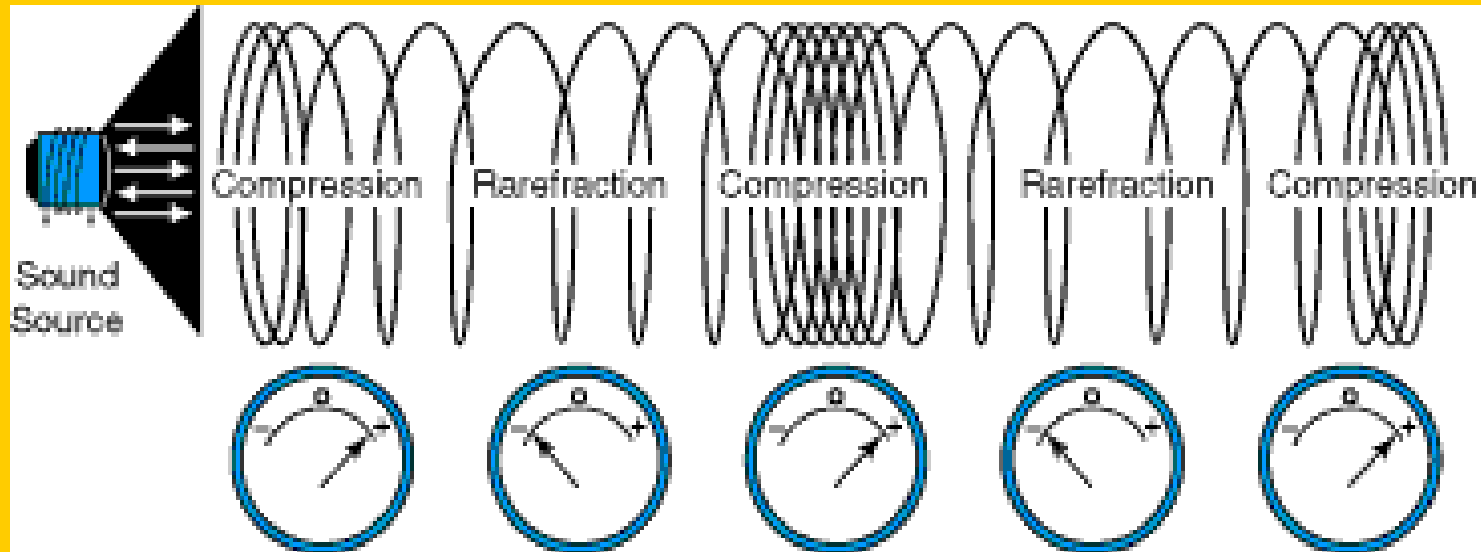
The energy is propagated as deformations (tensile/compressive stress) in the media

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

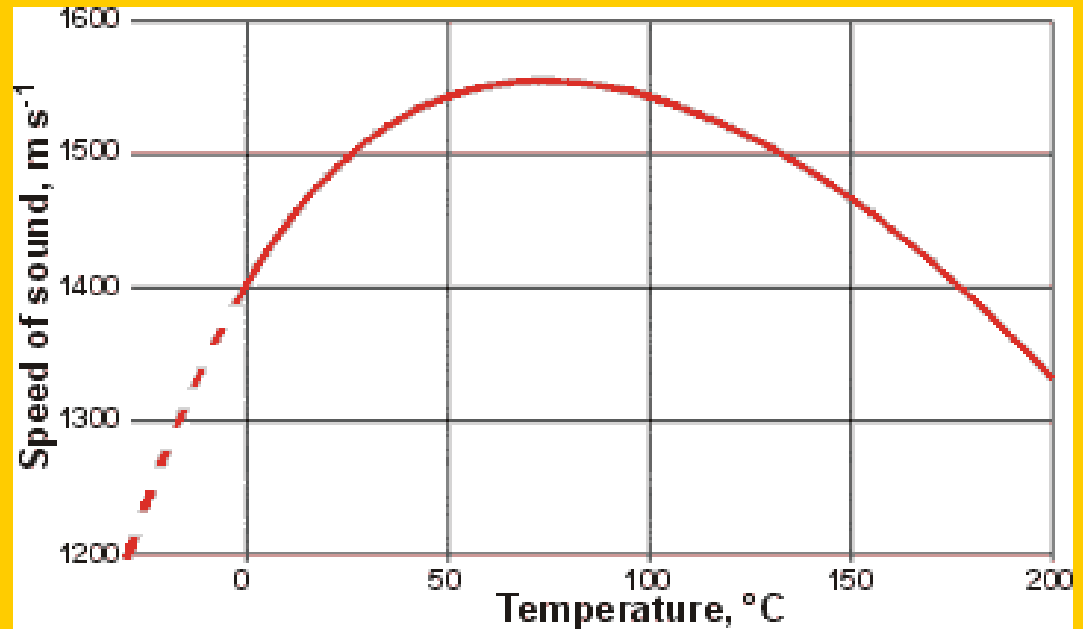
The speed of sound (u)

$$u^2 = 1/\kappa_S \rho = [\partial P / \partial \rho]_S \sim 1/(\langle (\nabla V)^2 \rangle)$$

κ_S = adiabatic compressibility

ρ = density

P = pressure



Sound Intensity

$$\text{Sound Intensity} = \text{Power} / \text{area} = \text{Watts/m}^2$$

<i>Source of Sound</i>	<i>Intensity (W/m²)</i>	<i>Sound level (dB)</i>
Jet Airplane 30 m away	10^2	140
Air-raid Siren, nearby	1	120
Threshold of Pain	10^{-1}	120
Concert	$\sim 10^{-1}$	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/m²)

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

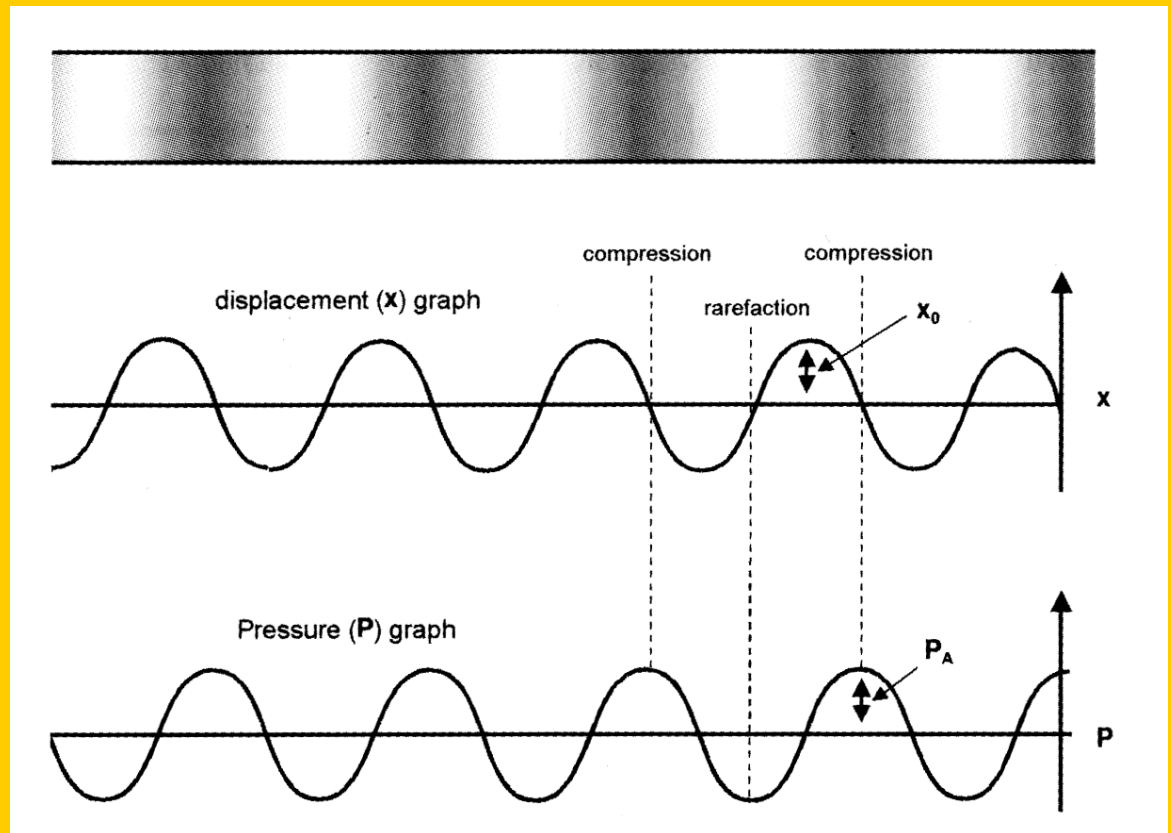
f sound frequency

$$c = \lambda f$$

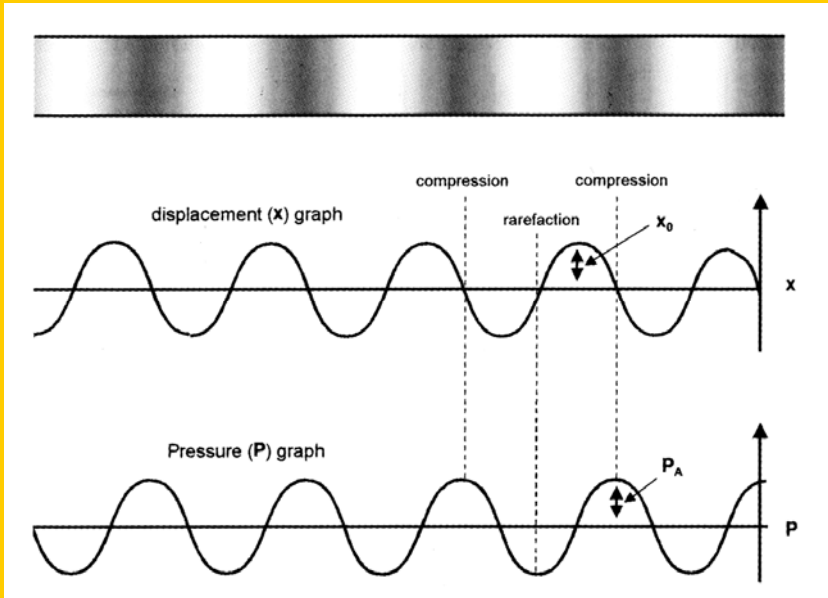
(for 20 kHz, $\lambda = 7.5$ cm)

$$P_{\text{total}} = P_a + P_h$$

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 - $1.3 \cdot 10^5 \text{ W m}^{-2}$)

ρ = liquid density [kg m^{-3}]

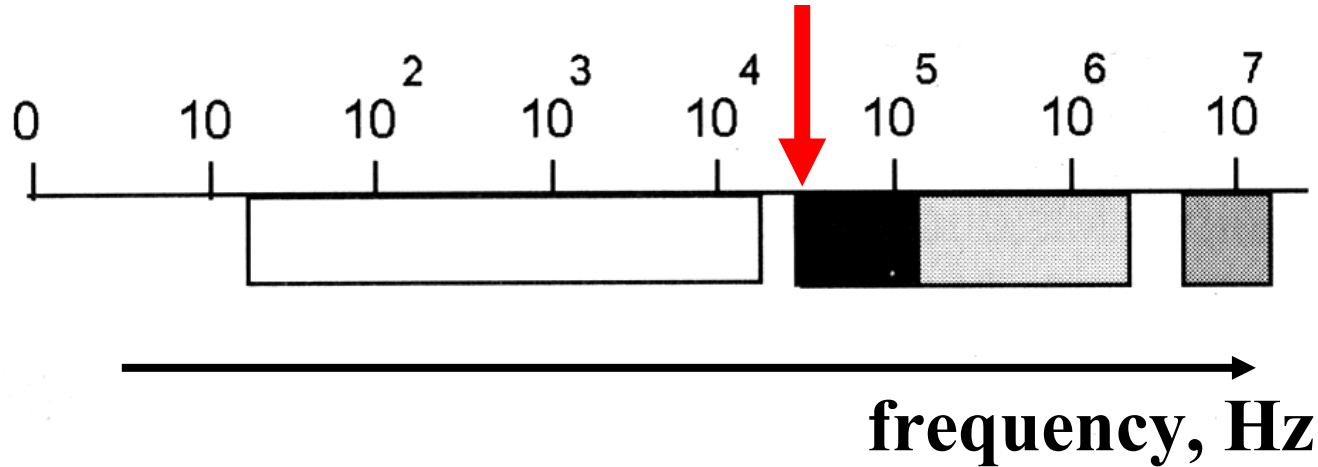
c = sound velocity in liquid [m s^{-1}]

(Water 1482 m s^{-1})

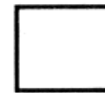
$$P_A = 620\,700 \text{ Pa} = 6.2 \text{ bar}$$

Ultrasound

Ultrasound frequencies from 20 kHz to 50 MHz



Human hearing



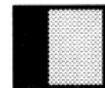
16Hz - 18kHz

Conventional power ultrasound



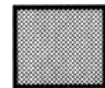
20kHz - 100kHz

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

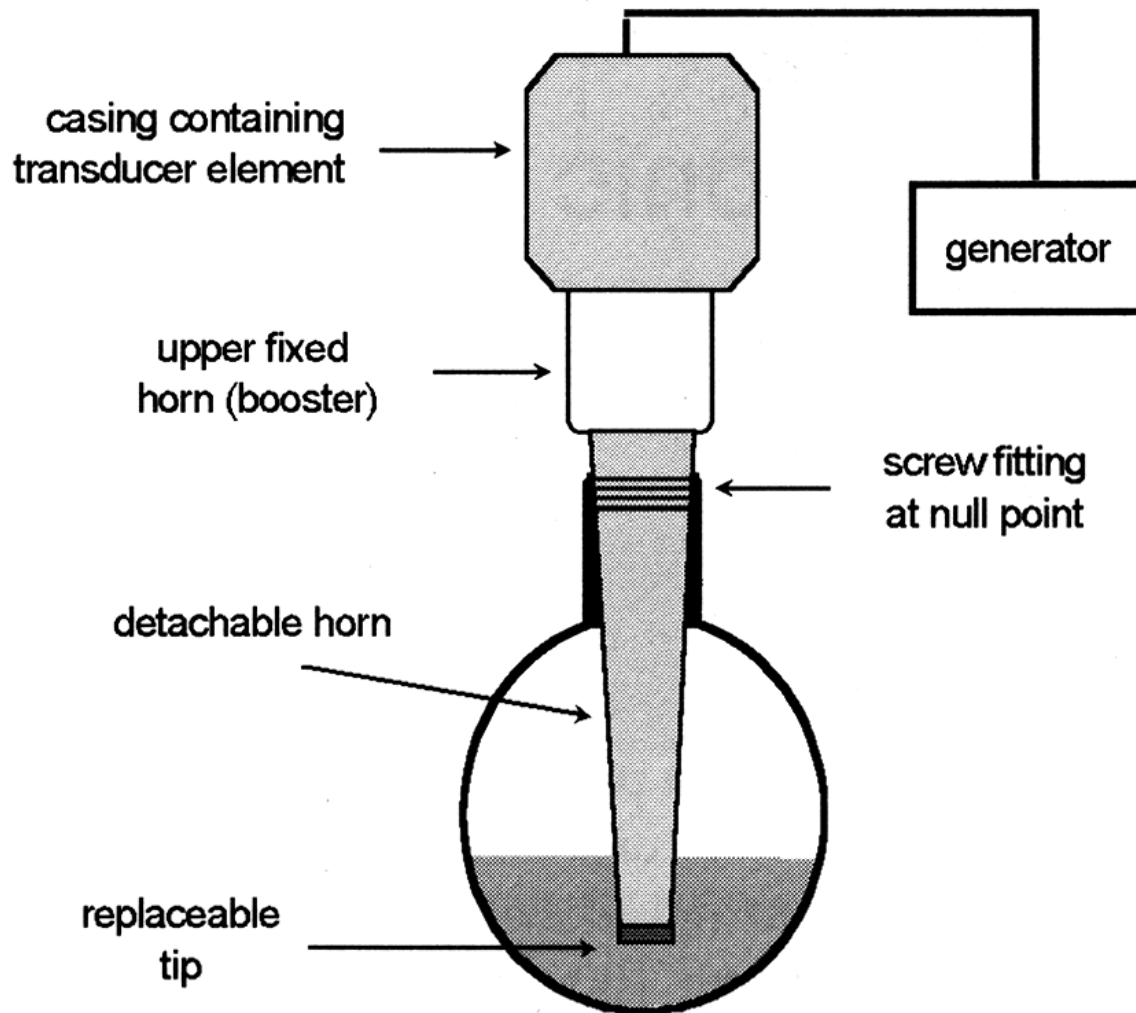
liquid whistle homogeniser, a jet of liquid passed through an orifice on a thin metal blade, vibrations, cavitation, mixing of immiscible liquids, ketchup, mayonnaise

electromechanical

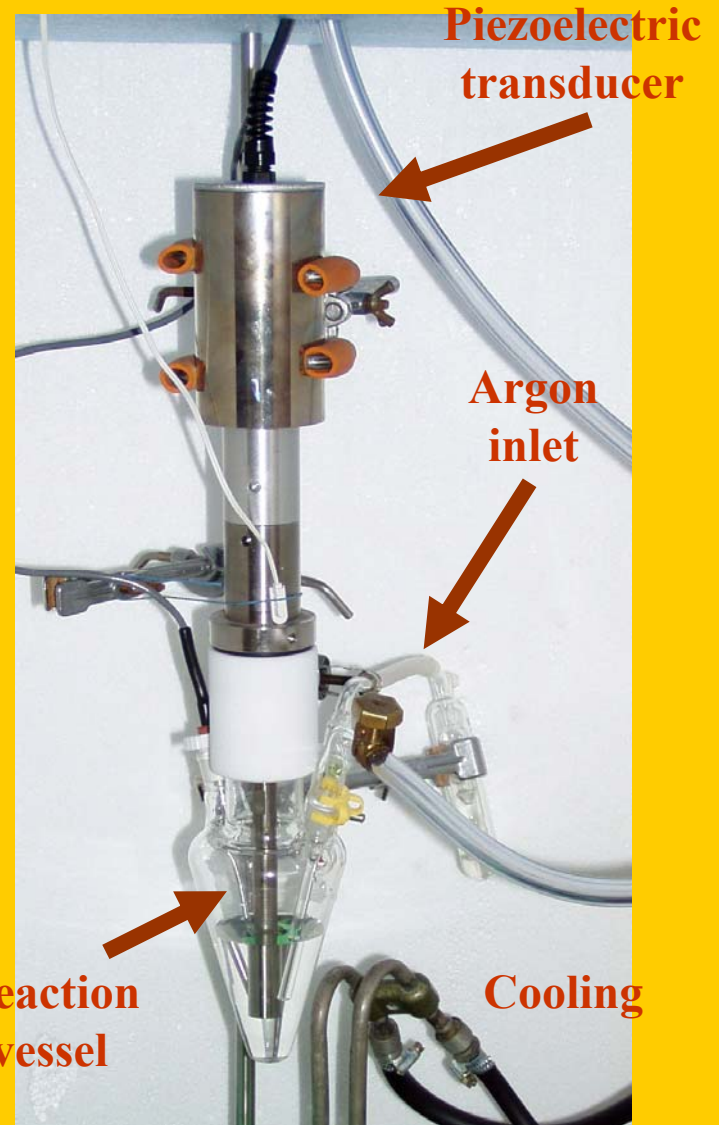
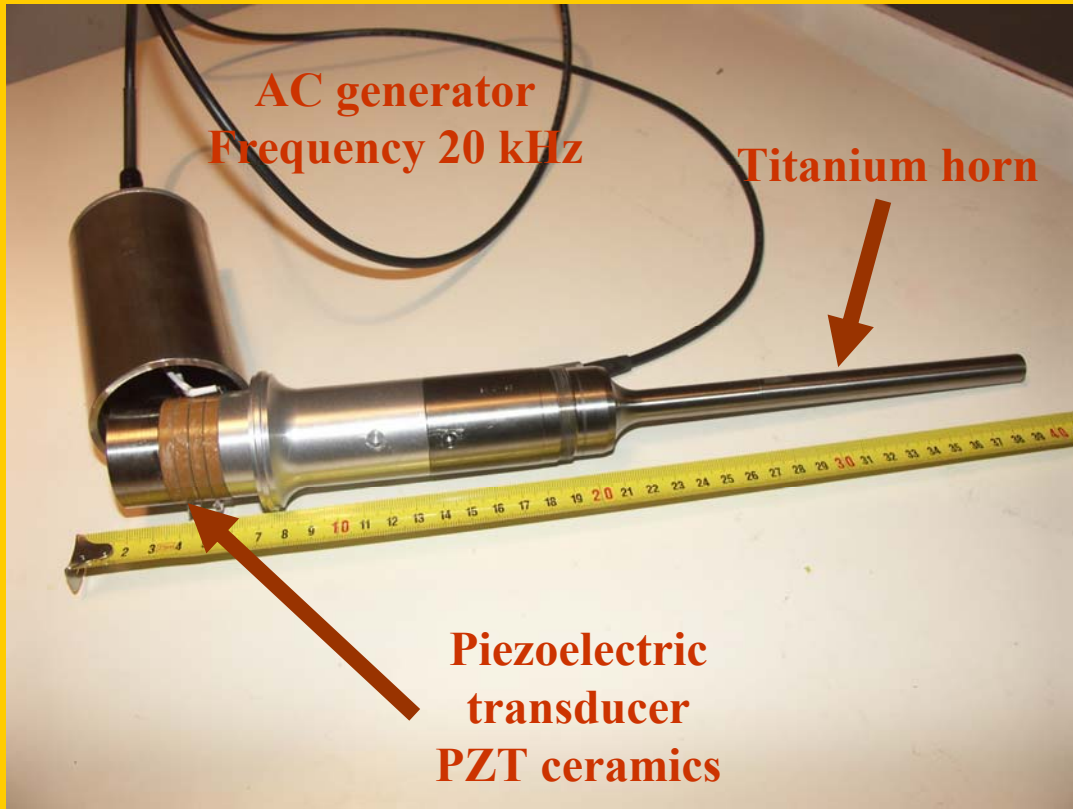
magnetostrictive, Ni, Co/Fe, Al/Fe, Tb/Dy/Fe alloys shrink when placed in mg. field, solenoid, pulses, upper limit 100 kHz, cooling

piezoelectric, opposite charges applied on crystal sides, contraction/expansion, quartz, $\text{Pb}(\text{Zr}/\text{Ti})\text{O}_3$ 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 cm³ min⁻¹)

TIME of ultrasound treatment

PULSE irradiation and a dwell time 2:2

TEMP maximum temperature 50 °C

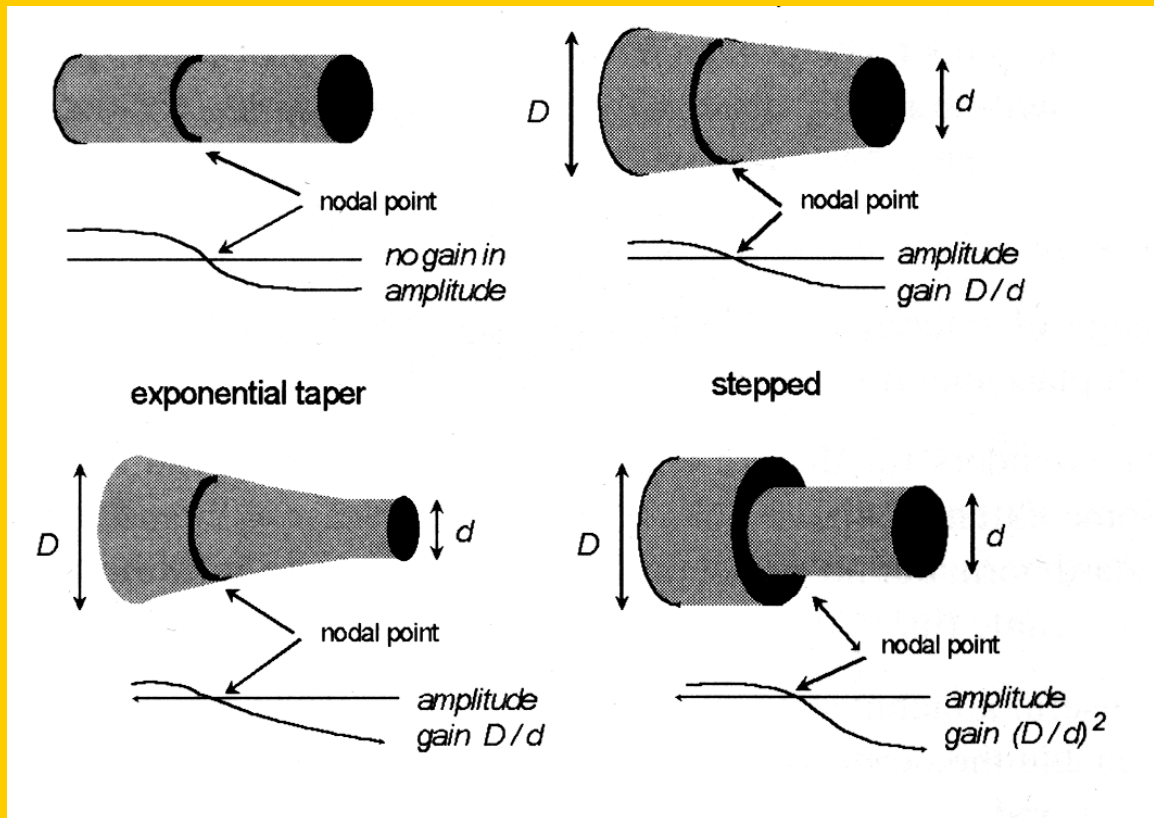
AMPL amplitude 50 %



Sonochemical Reactor

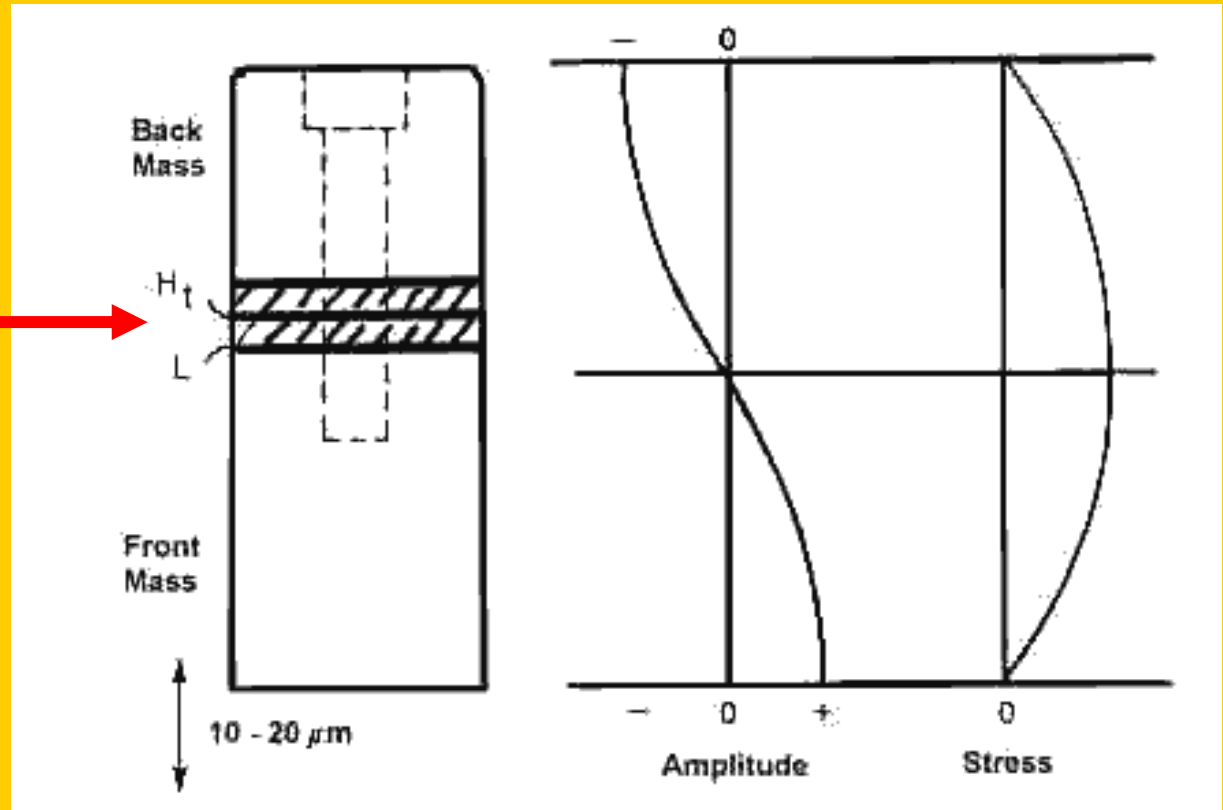
Ti alloy horn, minimum length is a half-wavelength of sound in a material, 26 cm for 20 kHz in Ti, multiples of 13 cm

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

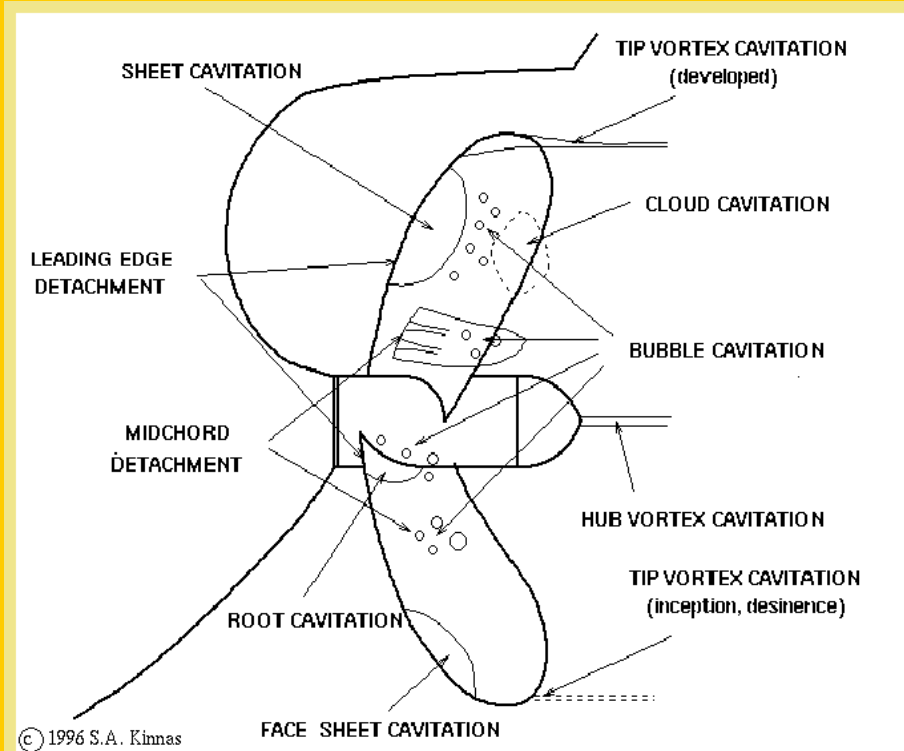
Hydrodynamic Cavitation

Lord Rayleigh for the British Admiralty 1895

cavitation erosion of propeller blades



$$R \ddot{R} + \frac{3}{2} \dot{R}^2 = \frac{1}{\rho} [p_g - P_0 - P(t)] - 4v \frac{\dot{R}}{R} - \frac{2\sigma}{\rho R}$$



The University of Texas at Austin

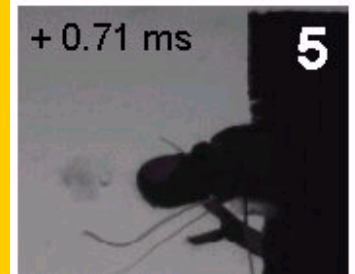
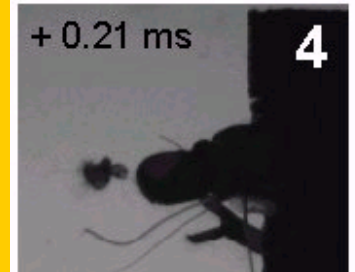
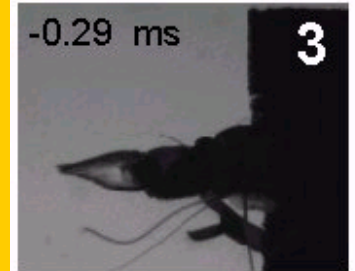
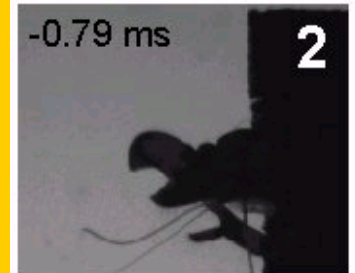
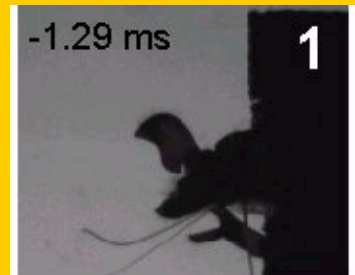
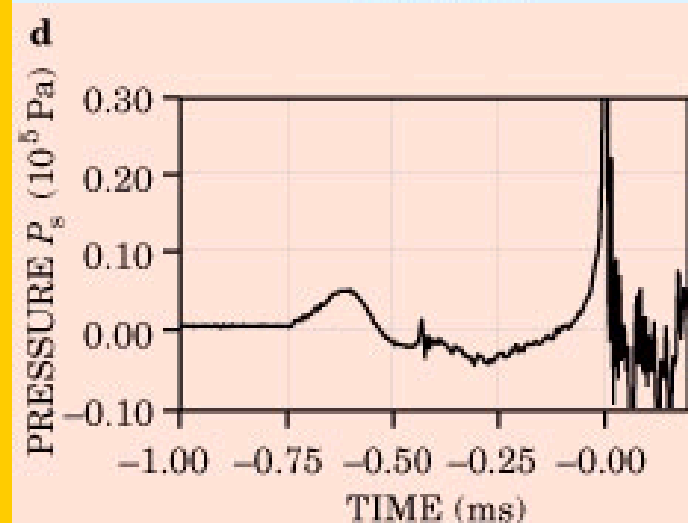
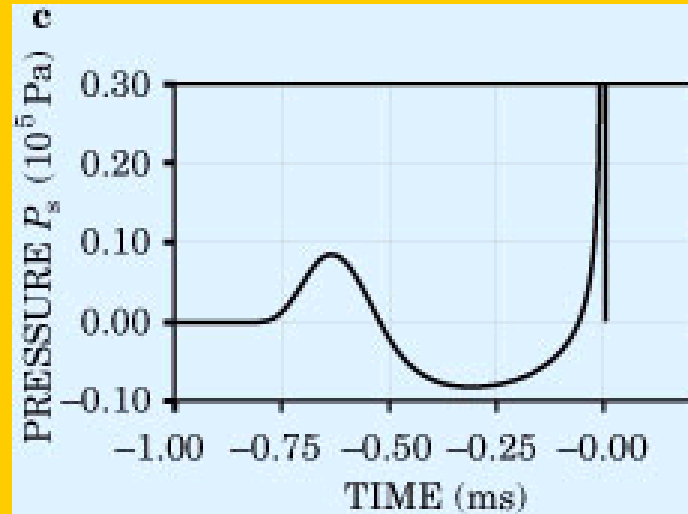
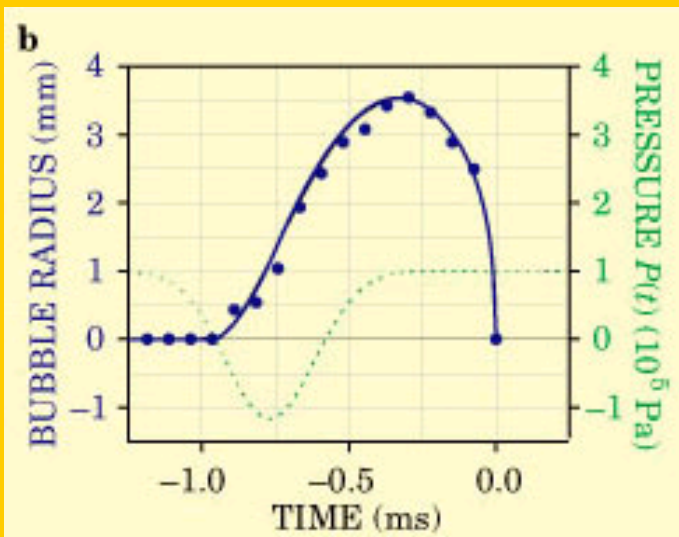
Snapping Shrimp

**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

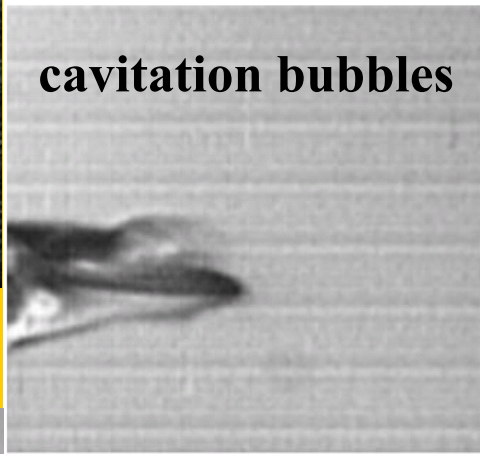


D. Lohse, B. Schmitz, M. Versluis, Nature 413, 477-478 (2001)

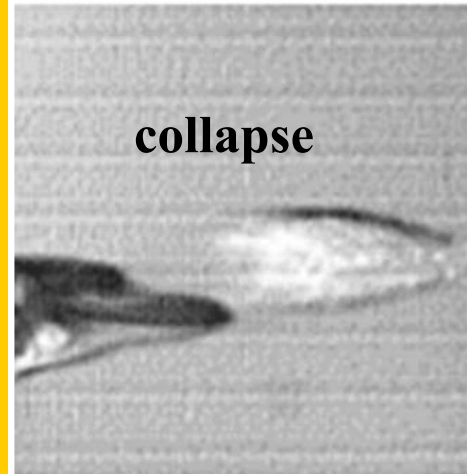
Snapping Shrimp



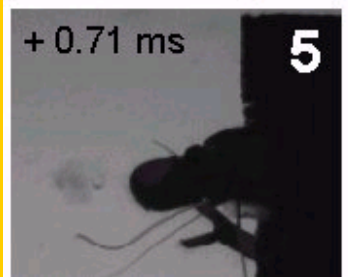
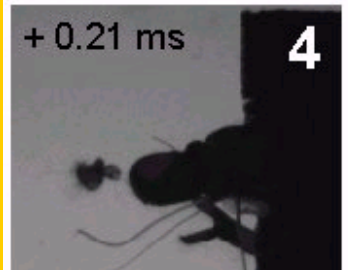
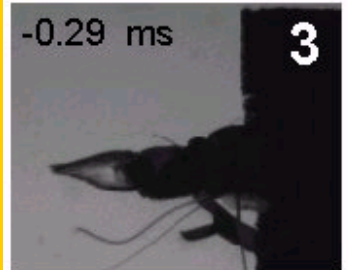
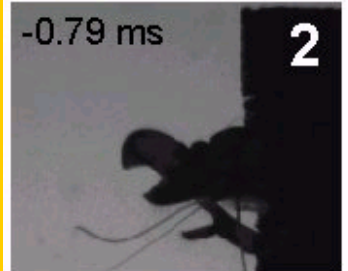
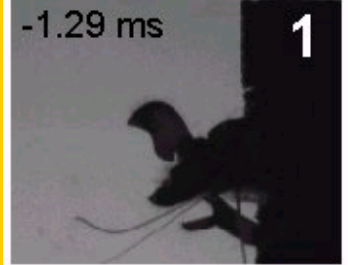
cavitation bubbles



collapse

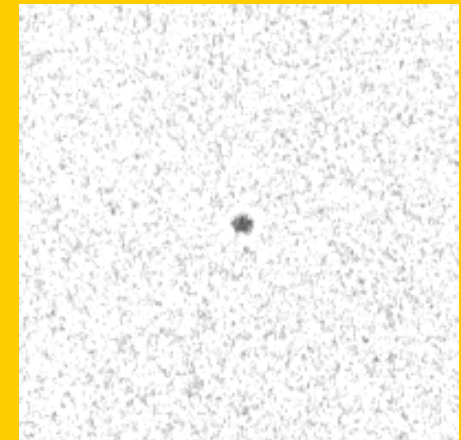
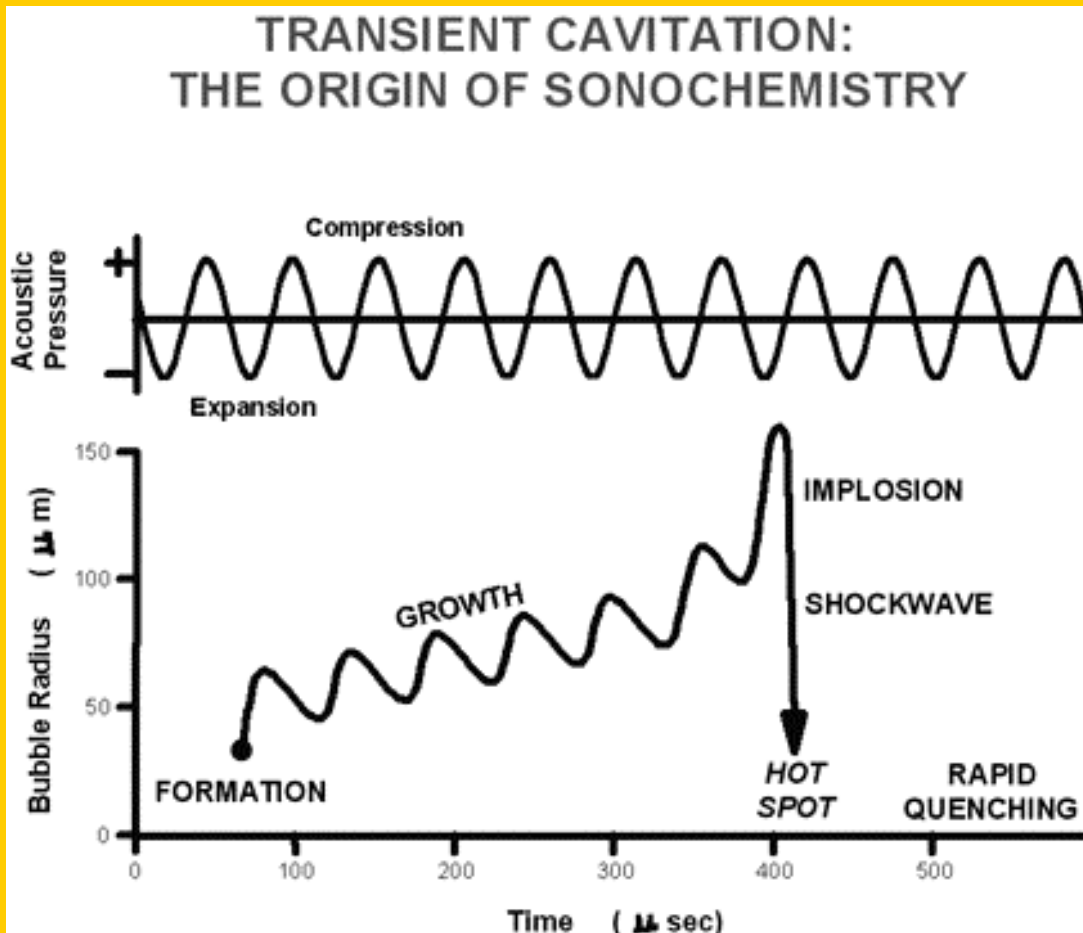


intense flash of light



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

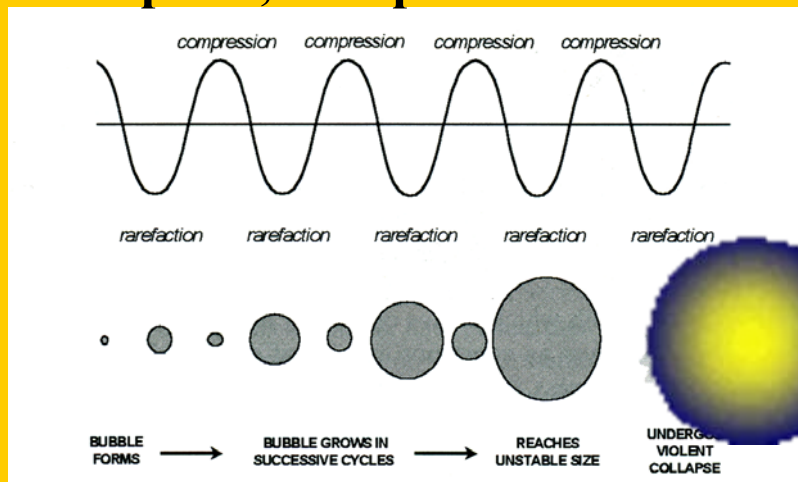
Acoustic Cavitation

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

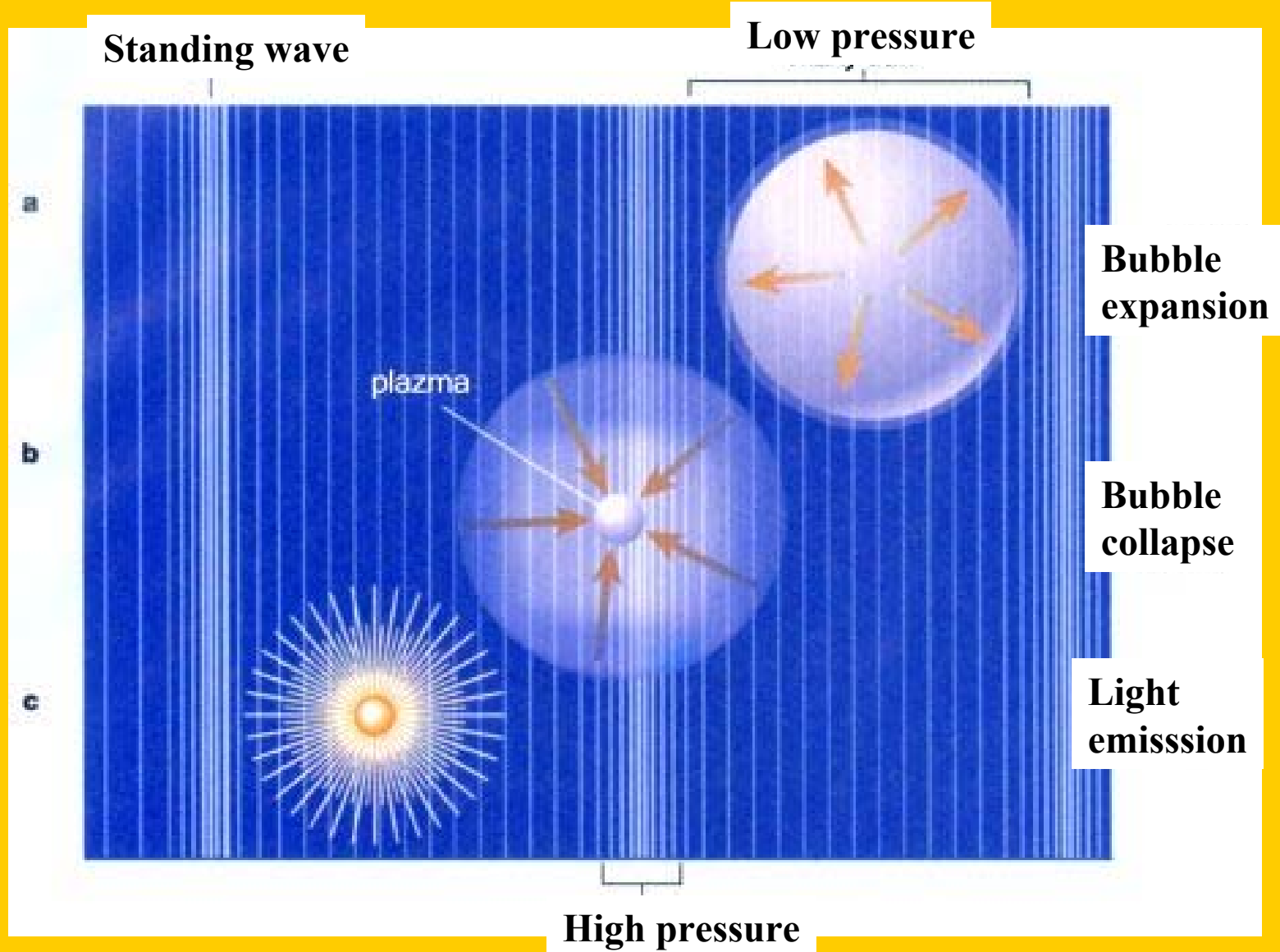
Bubble formation = breakage of liquid during **expansion, overcoming tensile strength (pure water 1500 bar, only 6.2 bar available)**

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



Acoustic Cavitation

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

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

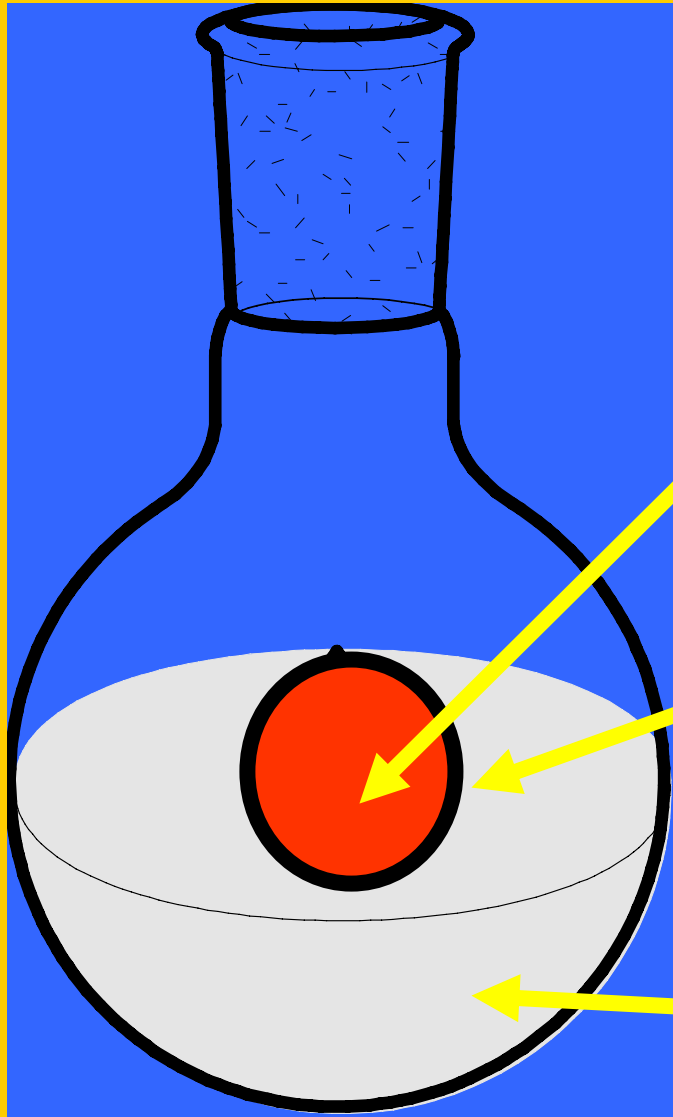
surrounding liquid layer 2000 °C

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



How to Measure the Temperature inside a Bubble ?

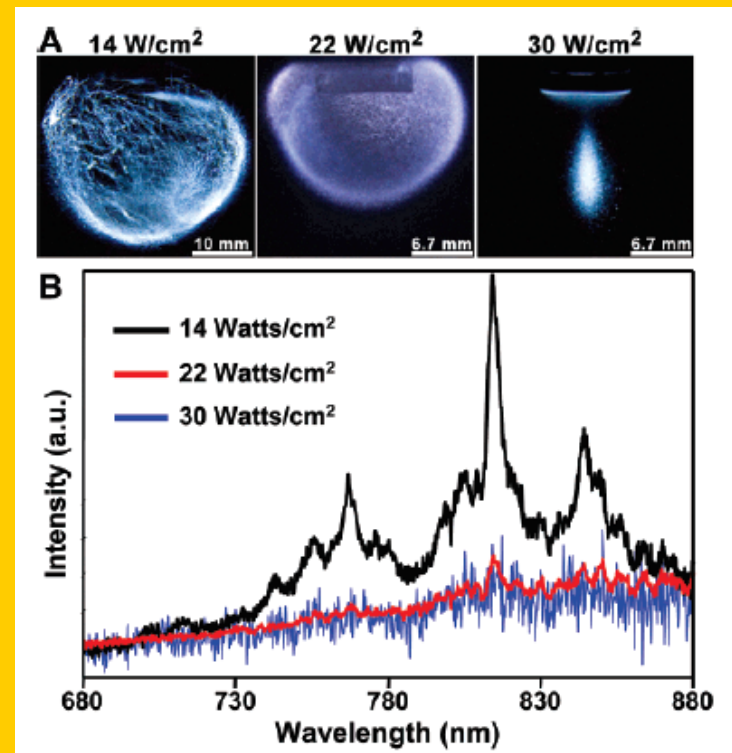
Sonoluminescence - Light generated during the implosive collapse of bubbles in liquids irradiated with ultrasound

95% H₂SO₄(aq.)
under Ar
20 kHz (14 W/cm²)
Ti horn directly immersed
T = 298 K

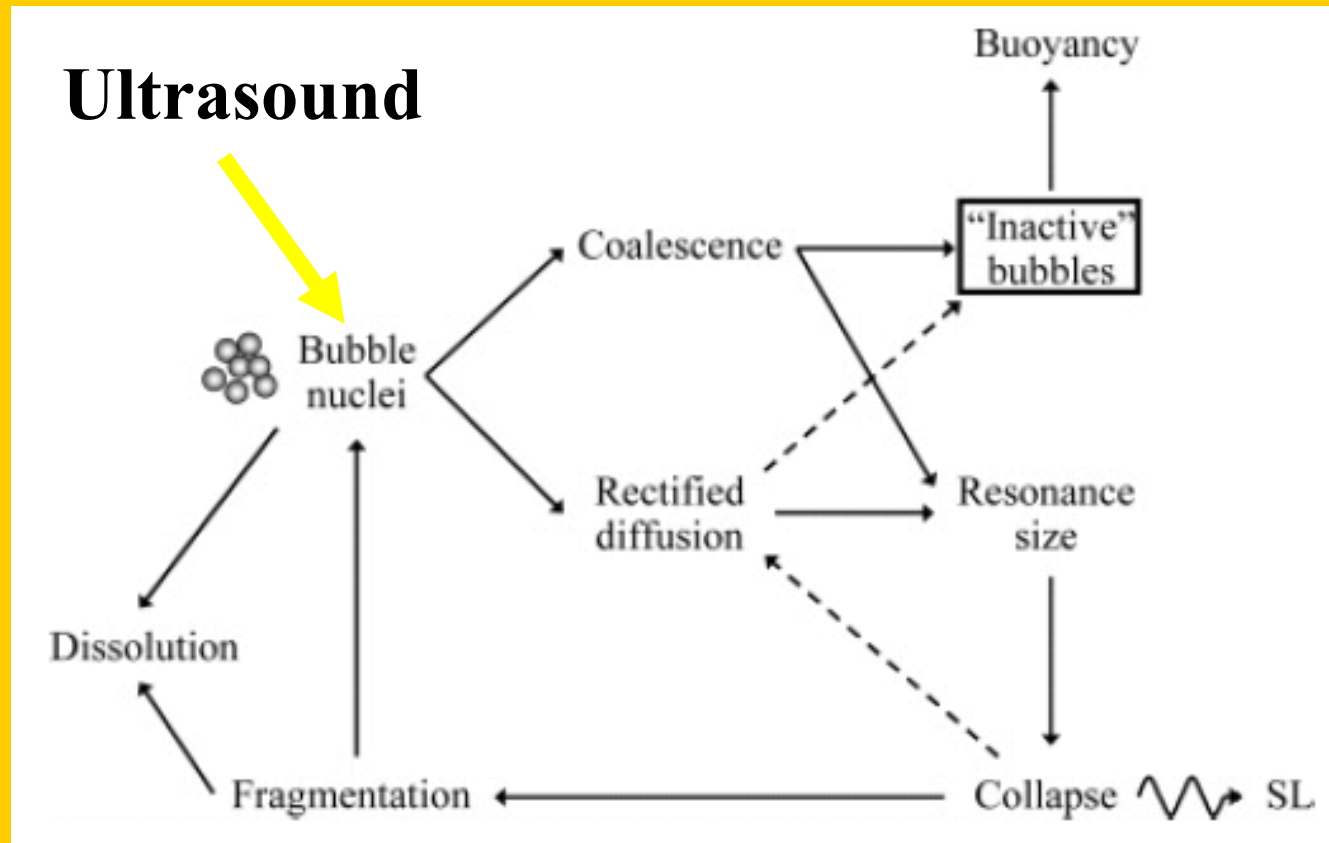
Kenneth S. Suslick
University of Illinois

- **Apparent blackbody temperature**
- **Ar emission**
- **SO and O₂⁺ emission**

8 000 – 15 000 K



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

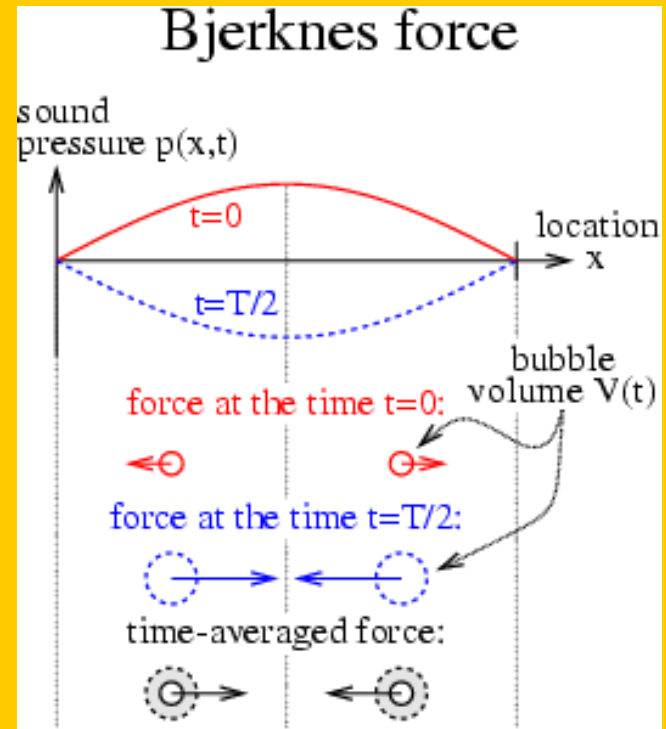
D. F. Gaitan, L. A. Crum, 1990

Standing acoustic wave field 1 bar

One bubble levitates in the acoustic field

The bubble oscillates for many cycles

Bubble sonoluminescence

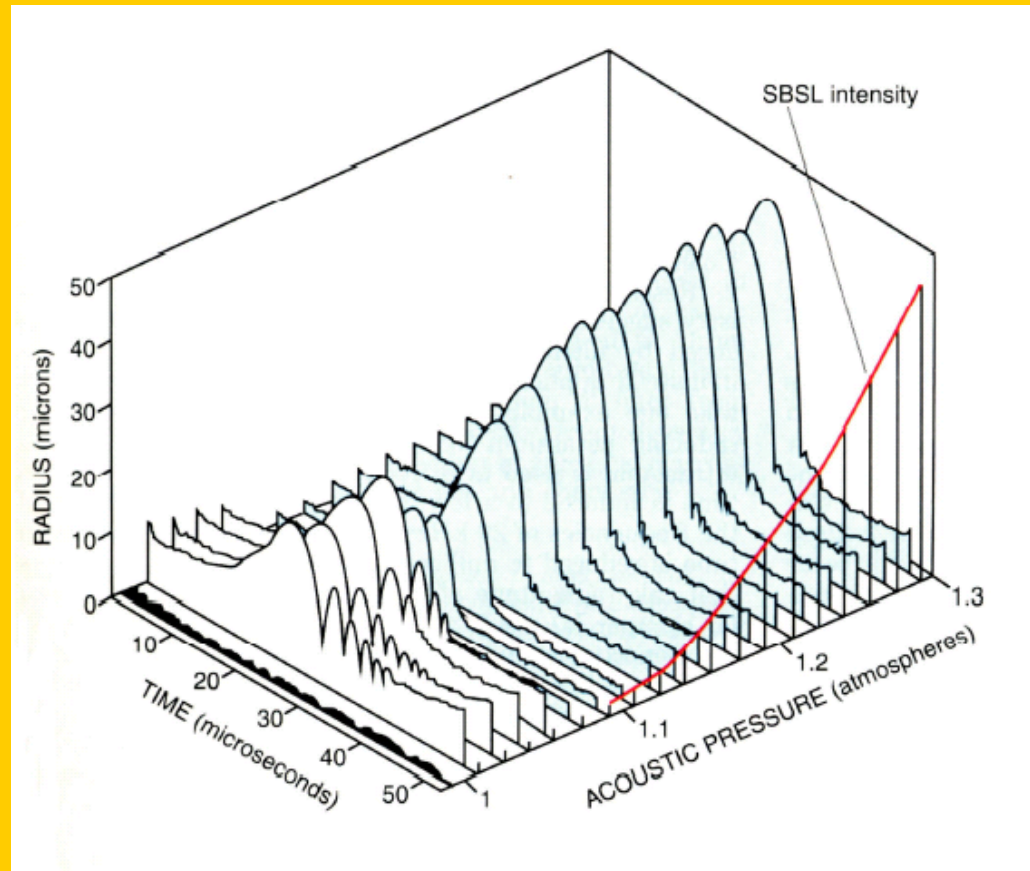


C. A. and V. Bjerknes

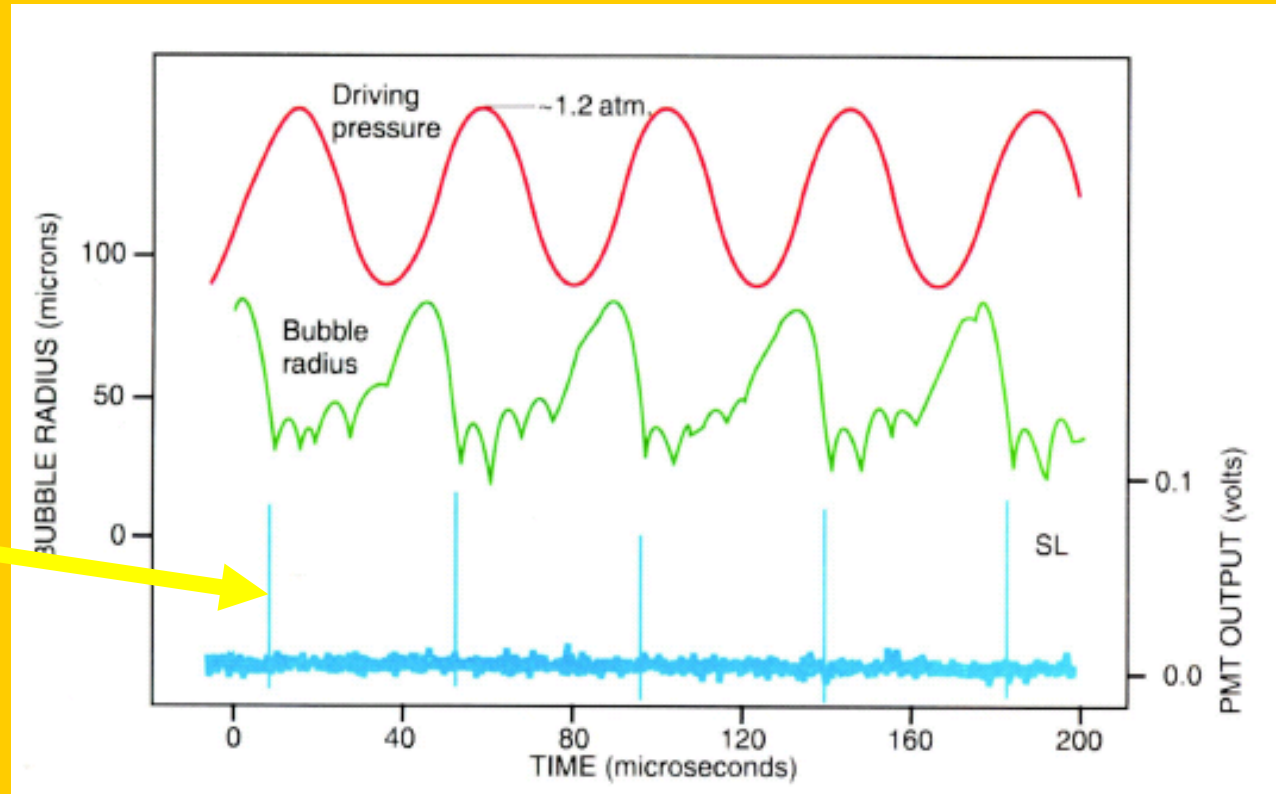
The force on an object in a liquid depends on its volume and the pressure gradient, the time averaged force drives the bubble towards the antinode of sound pressure and keeps it there.

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**

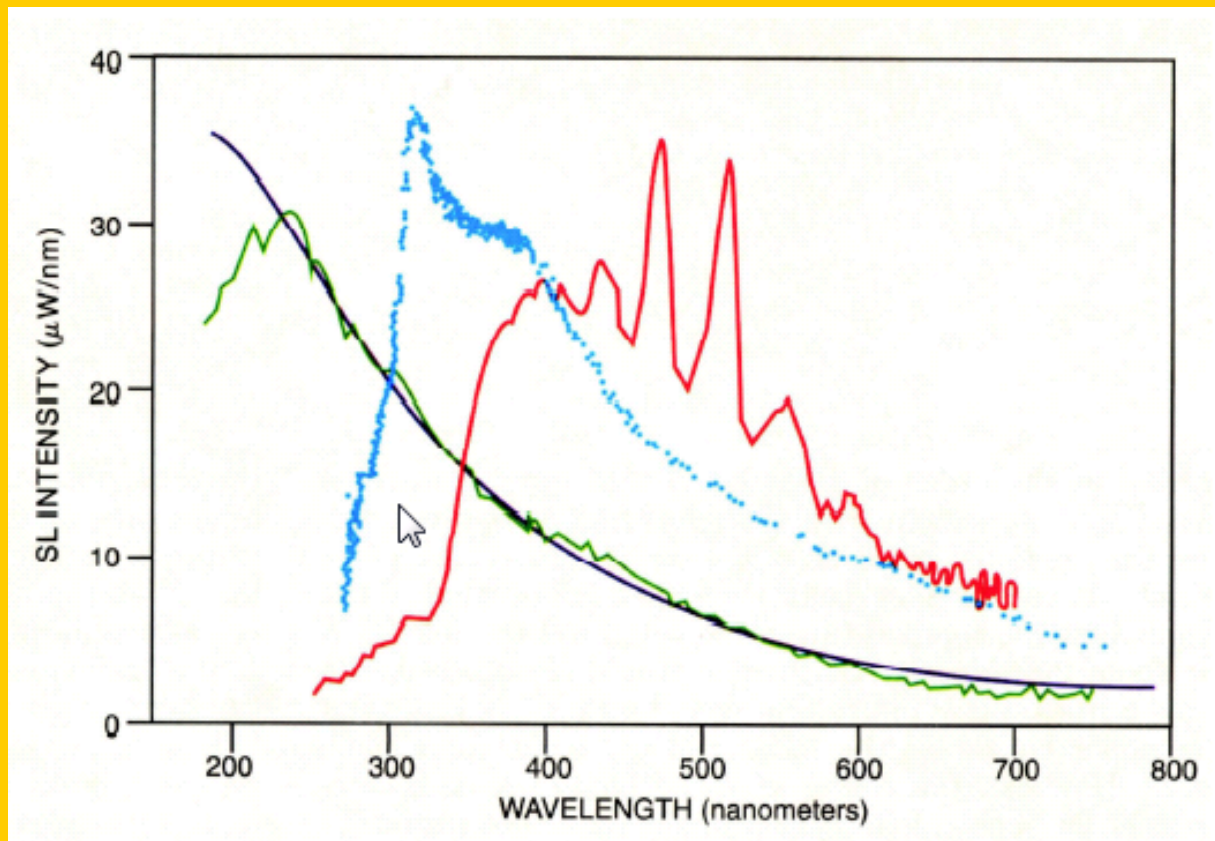
Single Bubble Sonoluminescence SBSL

Red – MBSL in dodecane

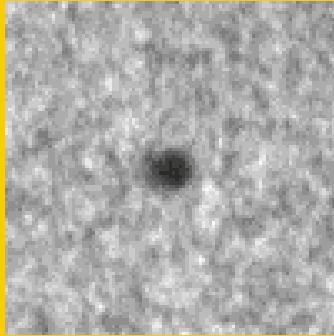
Blue – MBSL in water, 16 kHz

Green – SBSL in water, 43 kHz

Black – blackbody curve for 16200 K



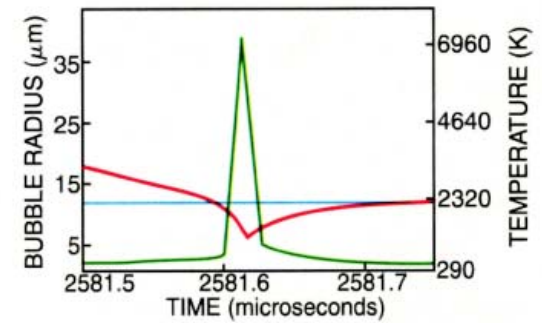
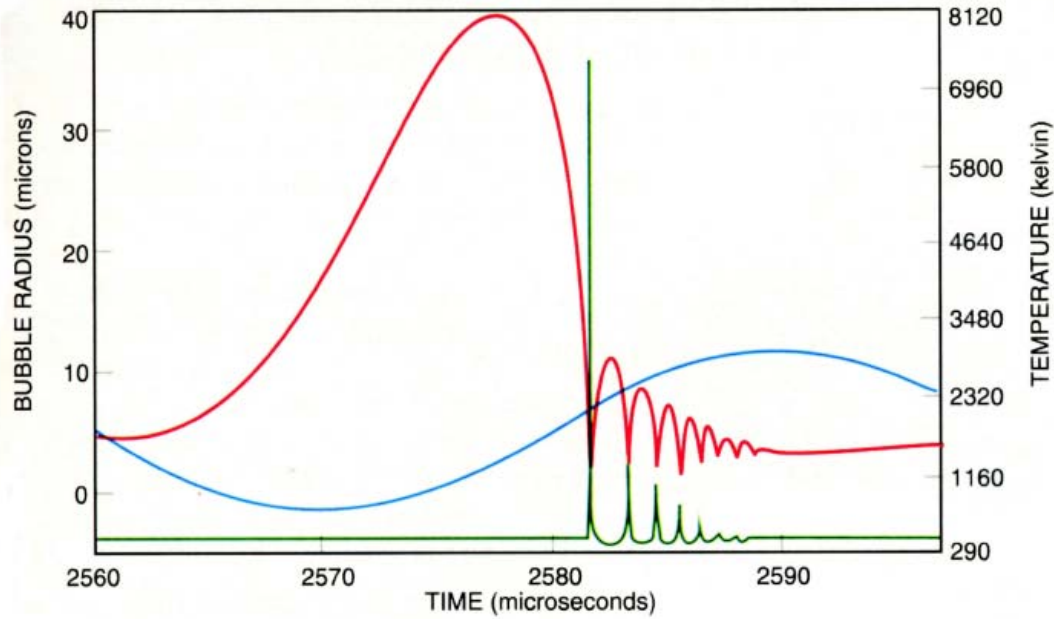
Single Bubble Sonoluminescence SBSL



Red - bubble radius

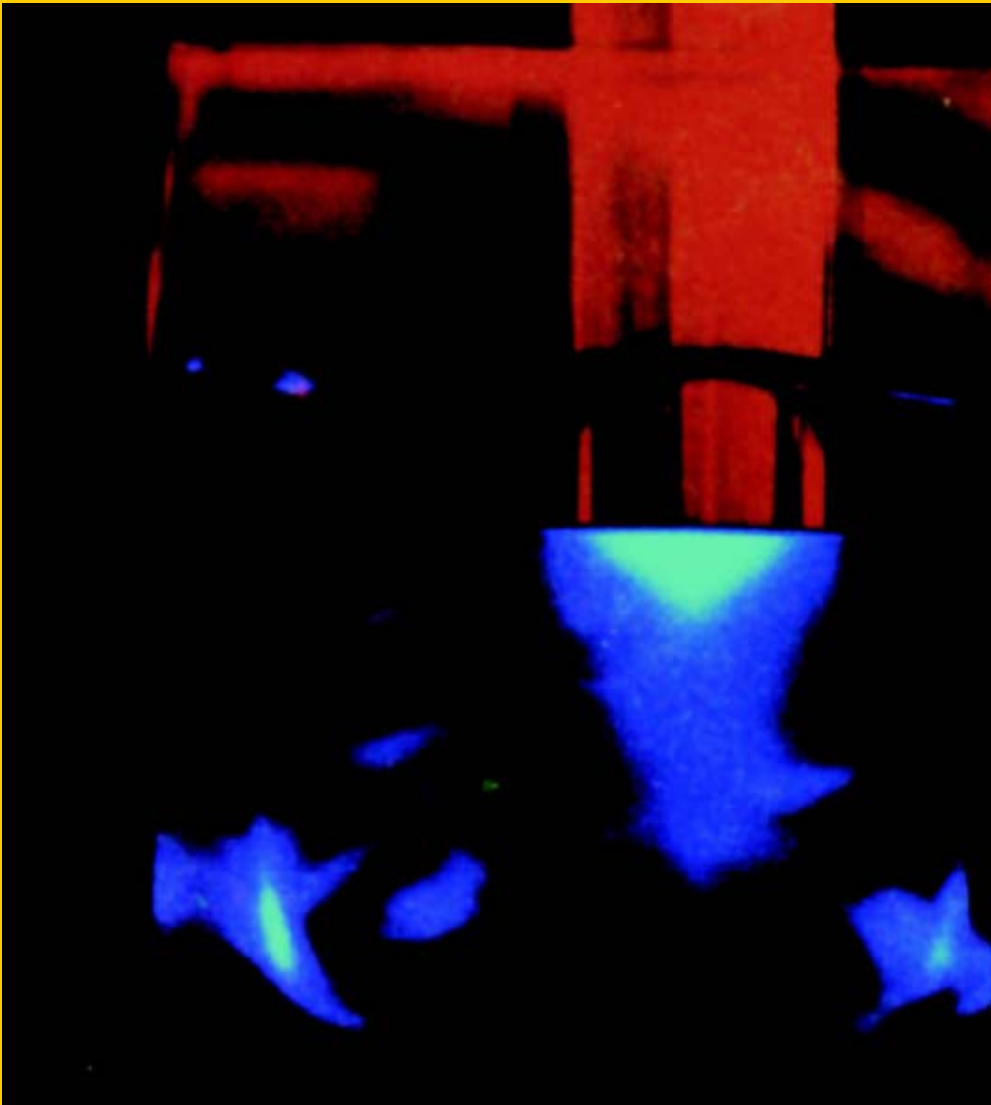
Green - bubble temperature

Blue - acoustic pressure 1.3 bar/25 kHz



Multi Bubble Sonoluminescence

MBSL



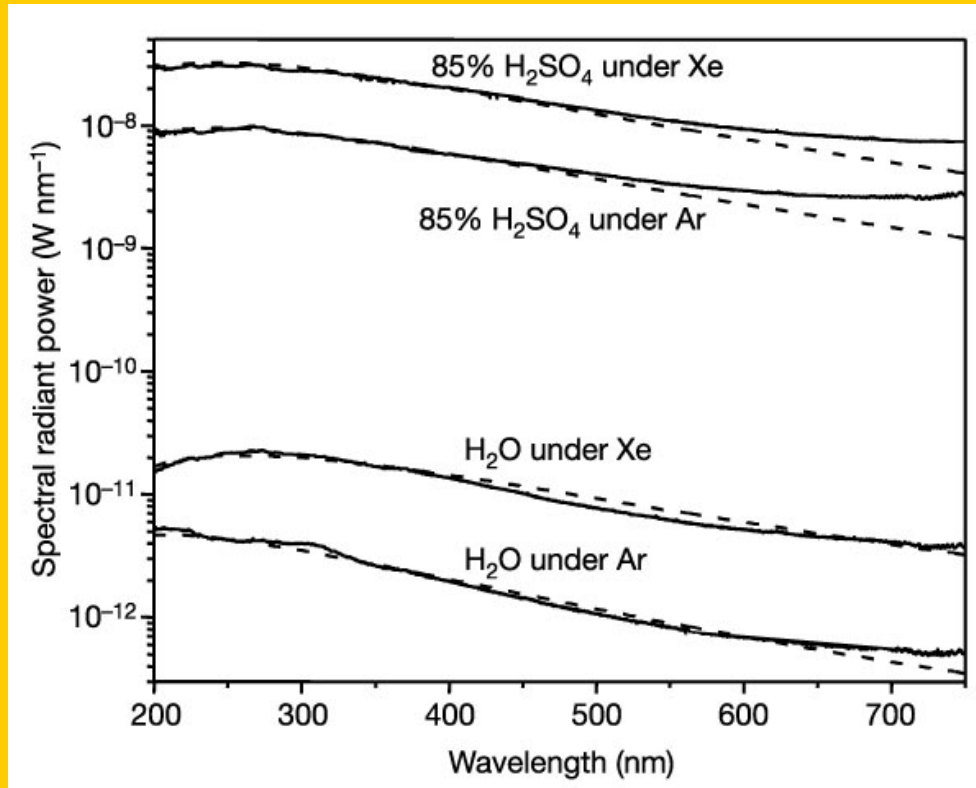
Multi-bubble sonoluminescence

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)

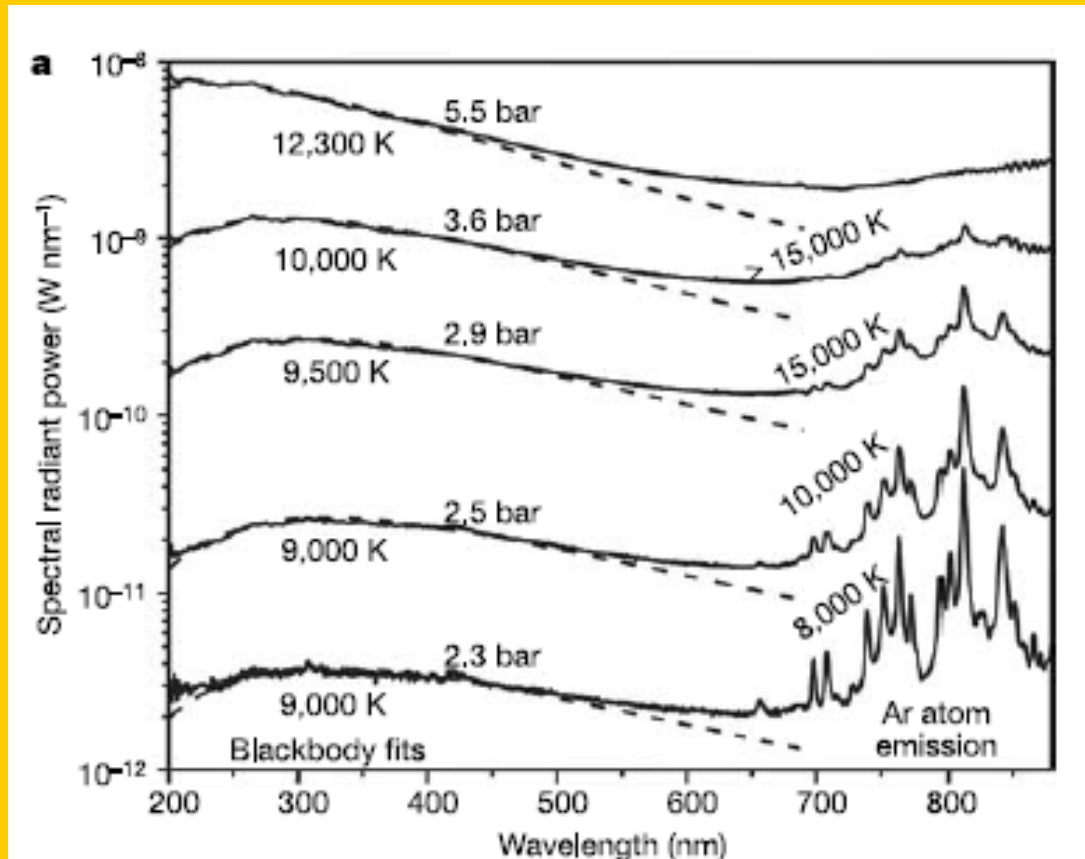
$12500 \pm 1500 \text{ K}$

Sonoluminescence

95% H₂SO₄(aq.)

blackbody temperature

Ar emission

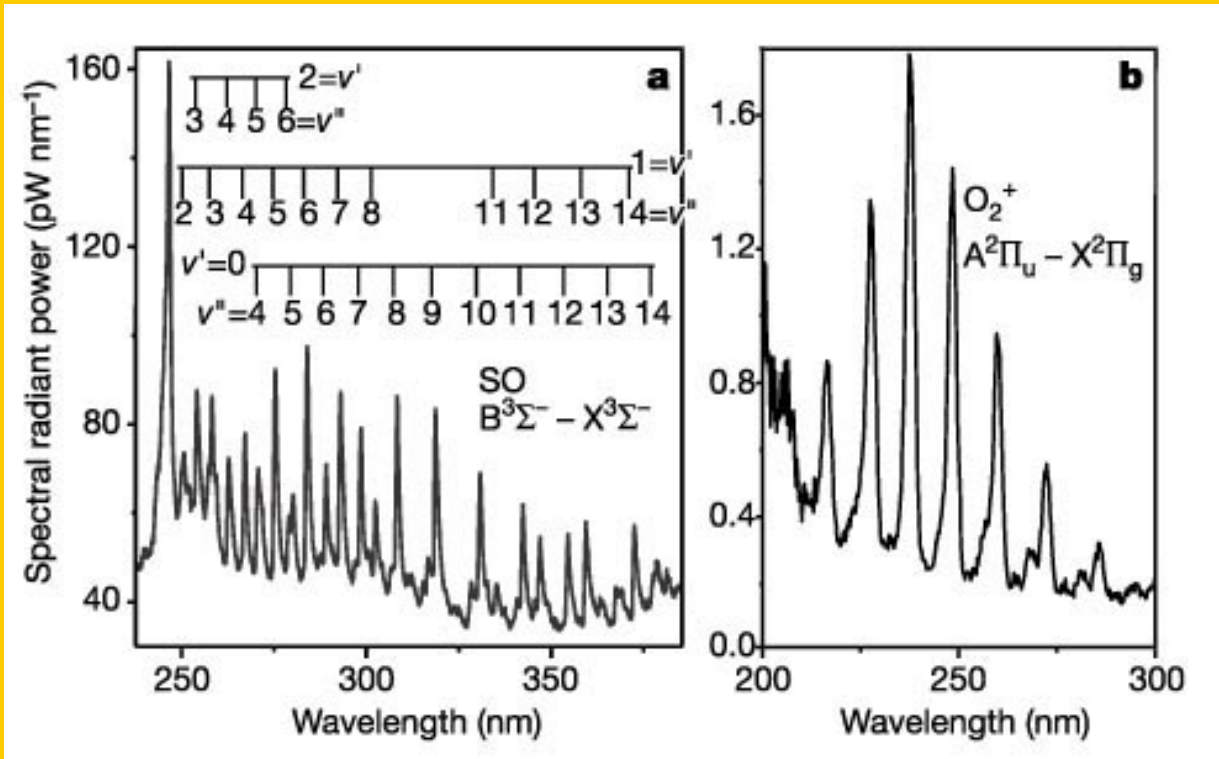


an optically
opaque
plasma core

Sonoluminescence

95% H₂SO₄(aq.)

SO and O₂⁺ emission
with vibronic progression

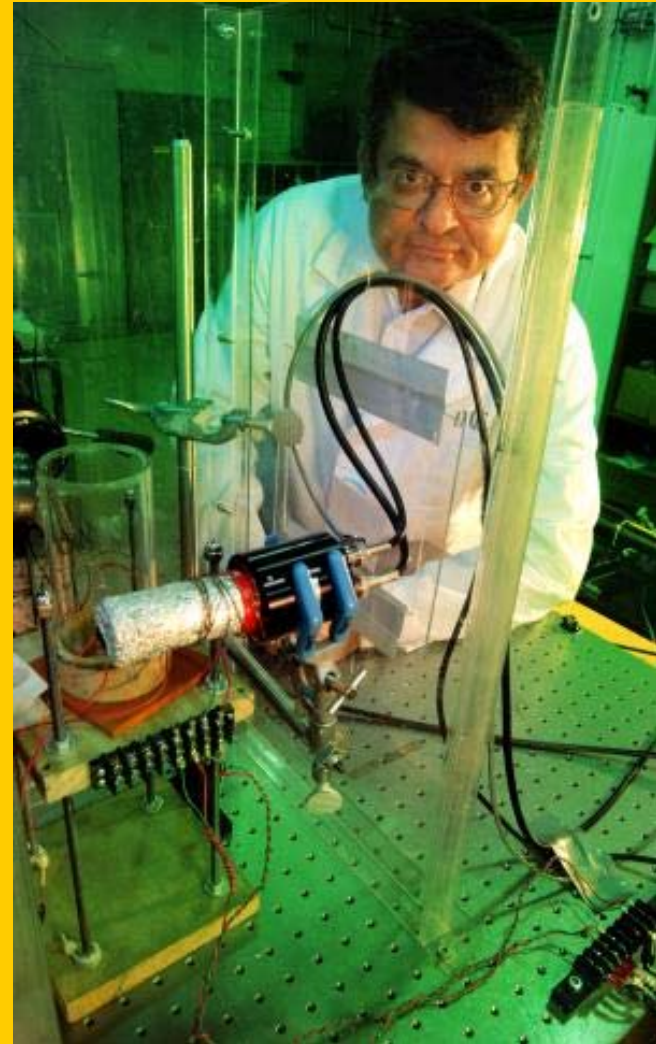
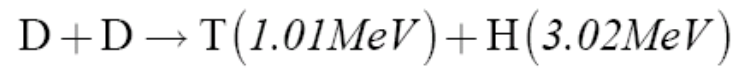


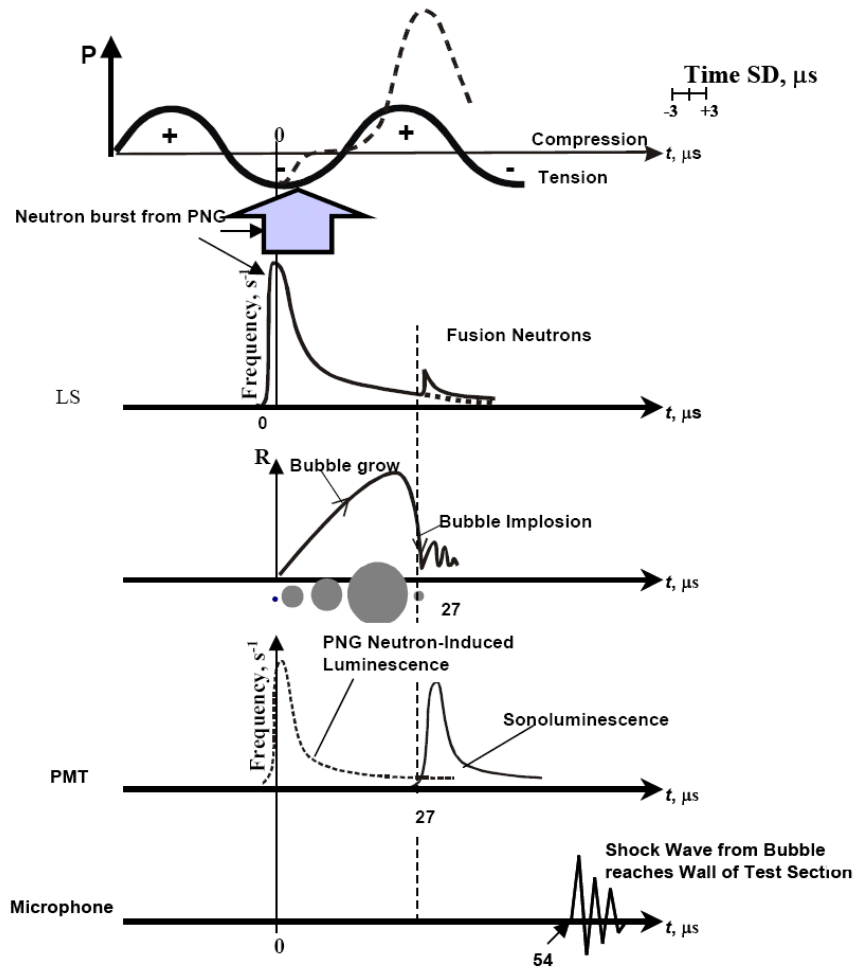
1580 ± 110 K at 3.3 bar

2470 ± 170 K at 4.2 bar

3480 ± 240 K at 5.1 bar

Sonofusion Fraud



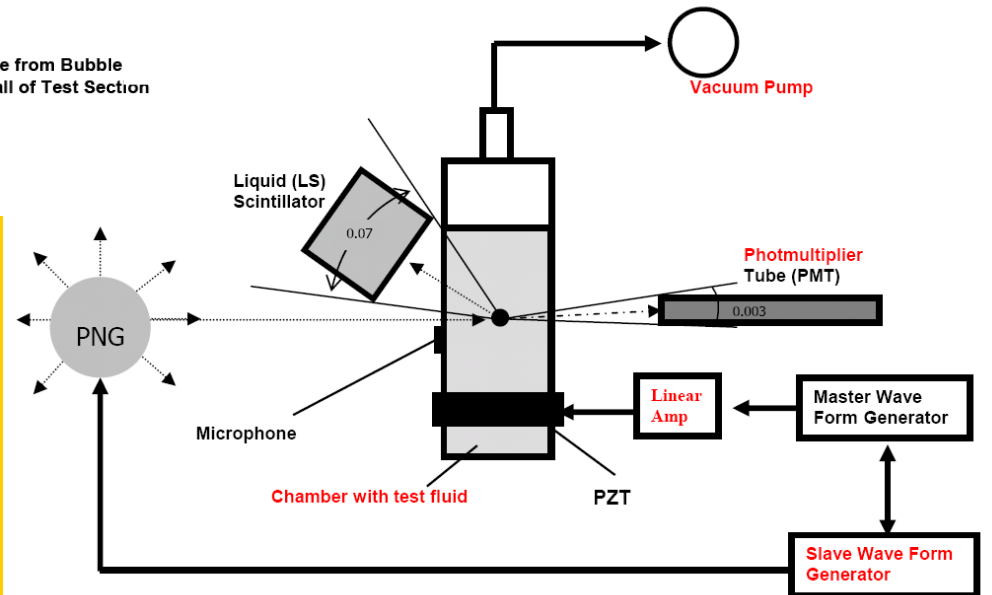


Sonofusion Fraud

Degassed deuterated acetone

$(CD_3)_2CO, 0\text{ }^\circ C$

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



Power Measurement in Sonochemistry

Calorimetry

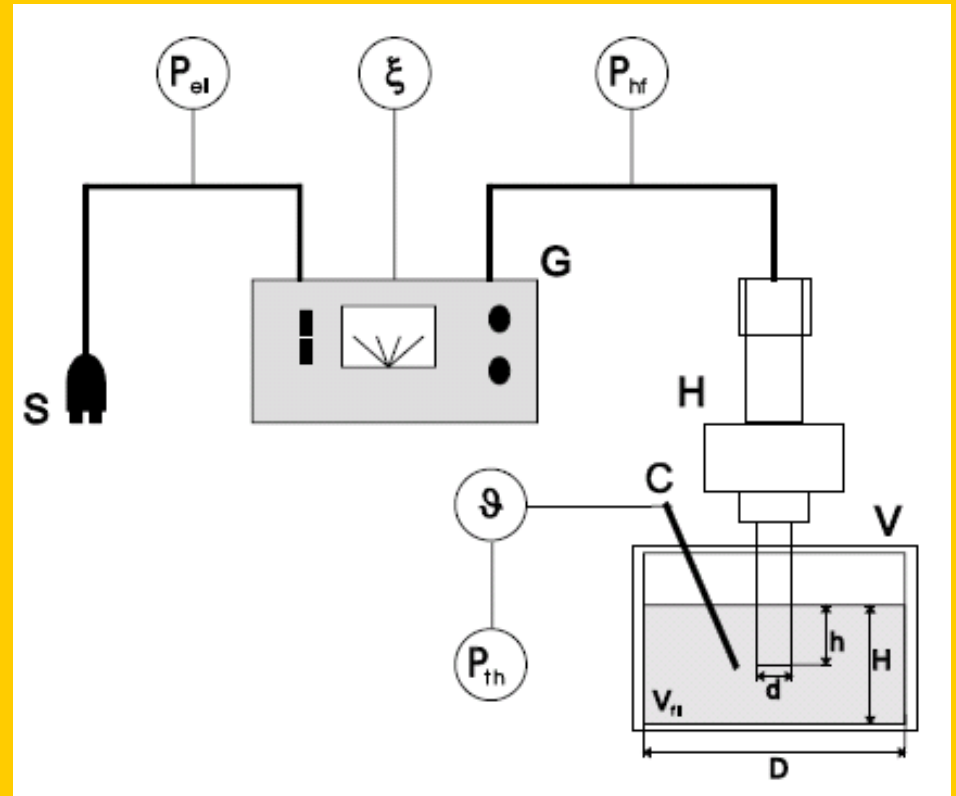
P = power, W

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

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

m = mass, g

Volume 50 cm³

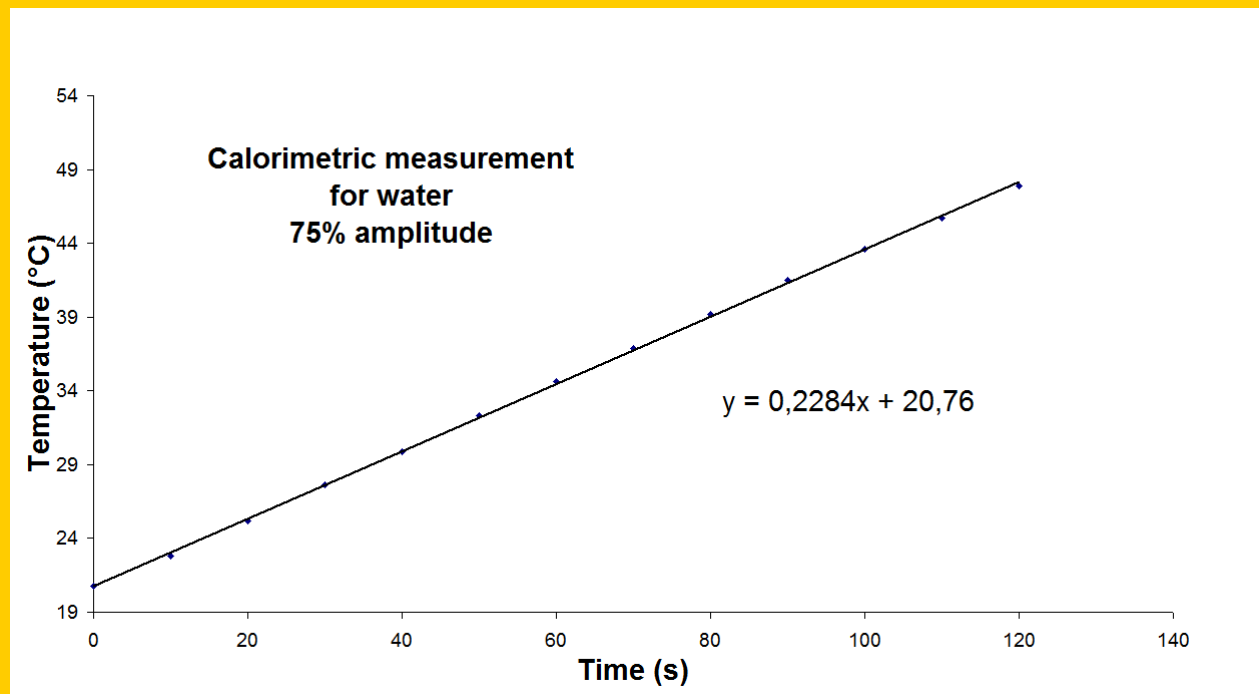
Argon atmosphere

Error 5%

heat capacity, J g⁻¹ K⁻¹

Water 4.2

Tetraglyme 2.08



Power Measurement in Sonochemistry

Chemical dosimetry

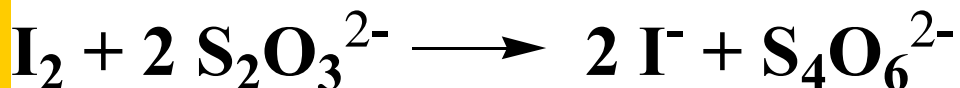
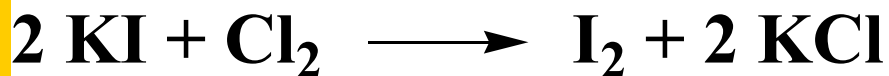
The Weissler reaction

Volume 50 cm³

KI 0.1 M

CCl₄ 0.2 cm³

Time 30 min

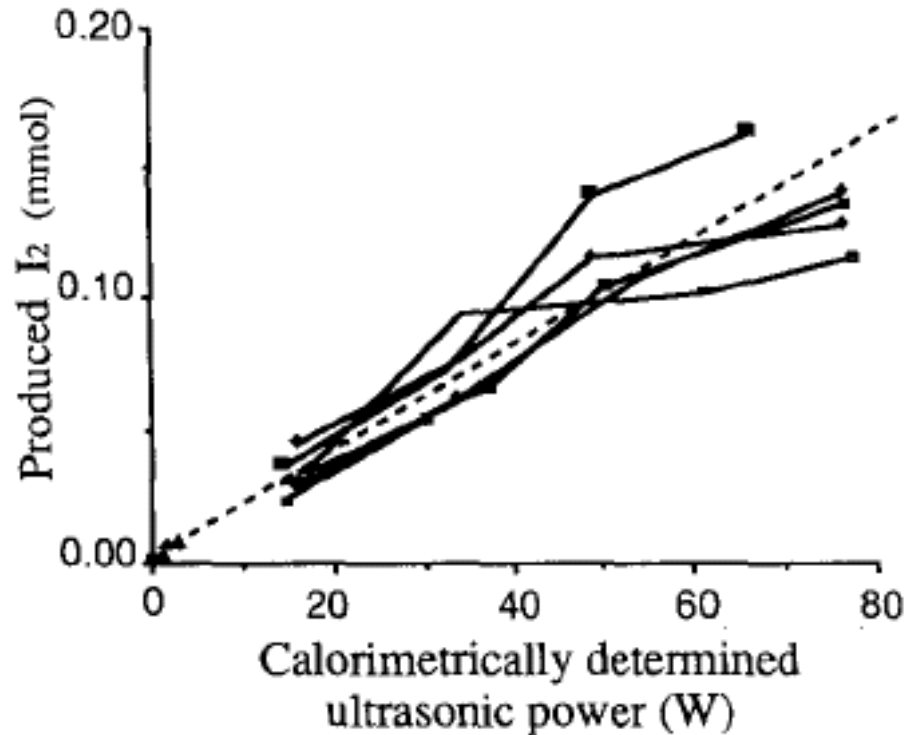
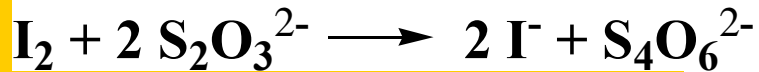
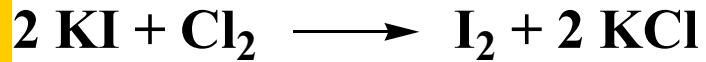


I₃⁻

$\lambda_{\text{max}} = 355 \text{ nm}$

$\epsilon = 26303 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$

Weissler Reaction



Power Measurement in Sonochemistry

Chemical dosimetry

The Fricke reaction

Volume 50 cm³

(NH₄) Fe(SO₄)₂·6H₂O

0.001 M

H₂SO₄ 0.4 M

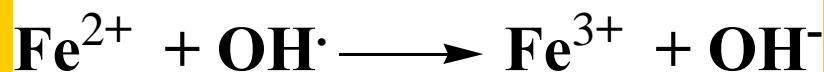
NaCl 0.001 M

Time 30 min

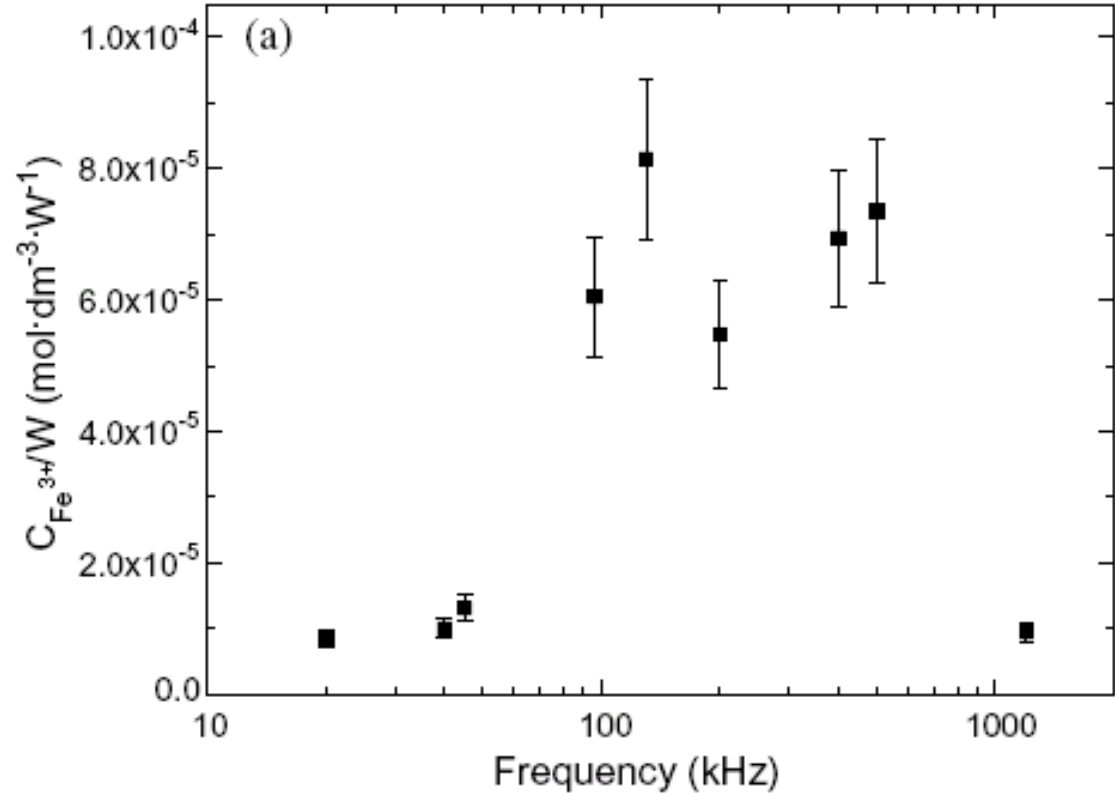
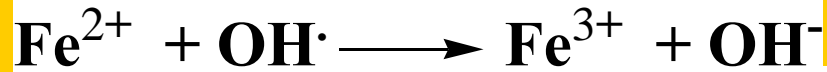
Fe³⁺

$\lambda_{\max} = 304 \text{ nm}$

$\epsilon = 2197 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$



Fricke Reaction



Power Measurement in Sonochemistry

Chemical dosimetry

Porphyrin decomposition ratio

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

TPPS

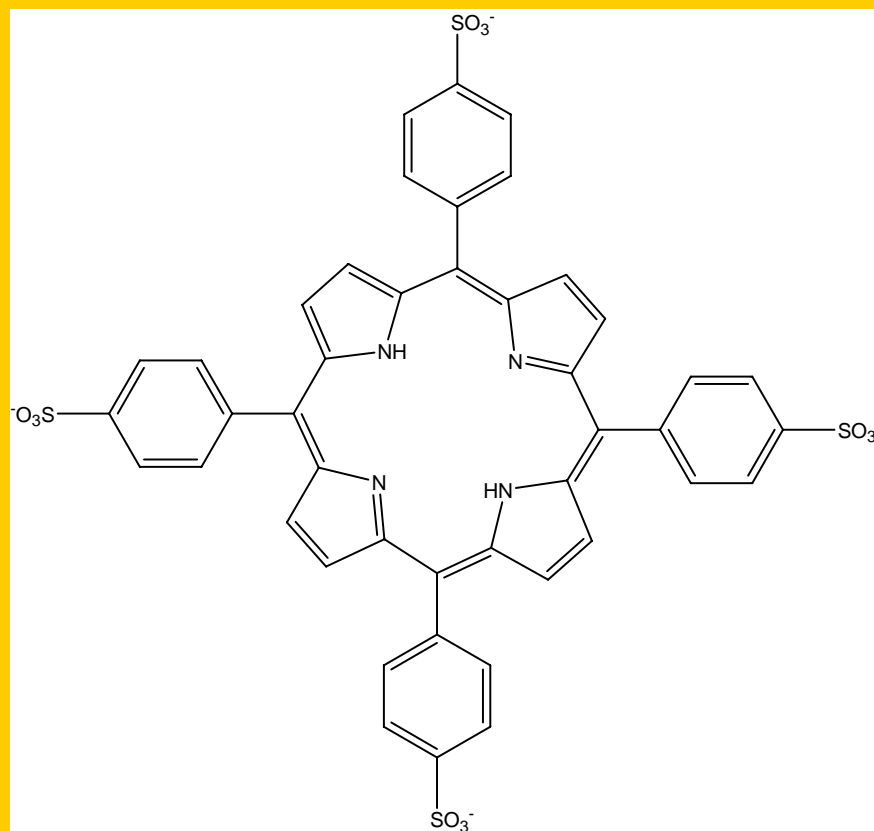
$3.3 \cdot 10^{-6} \text{ M}$

Volume 50 cm^3

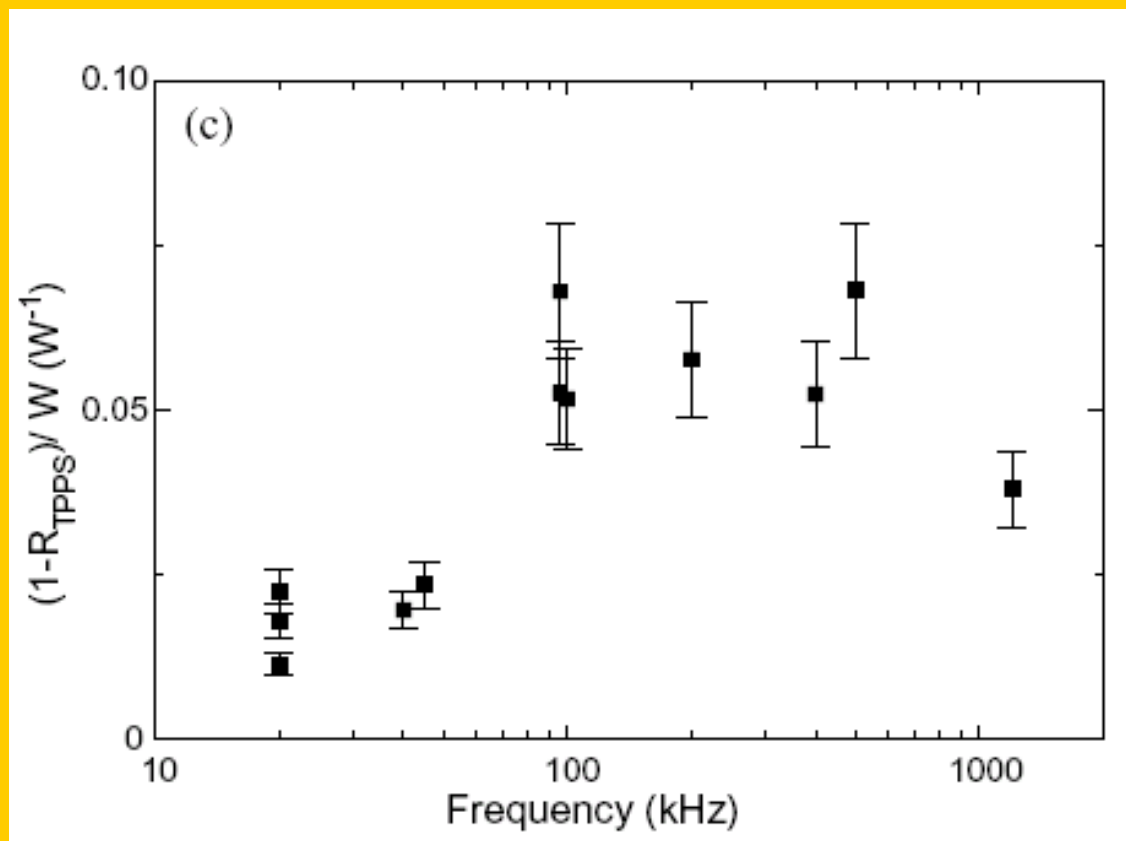
TPPS

$\lambda_{\text{max}} = 412 \text{ nm}$

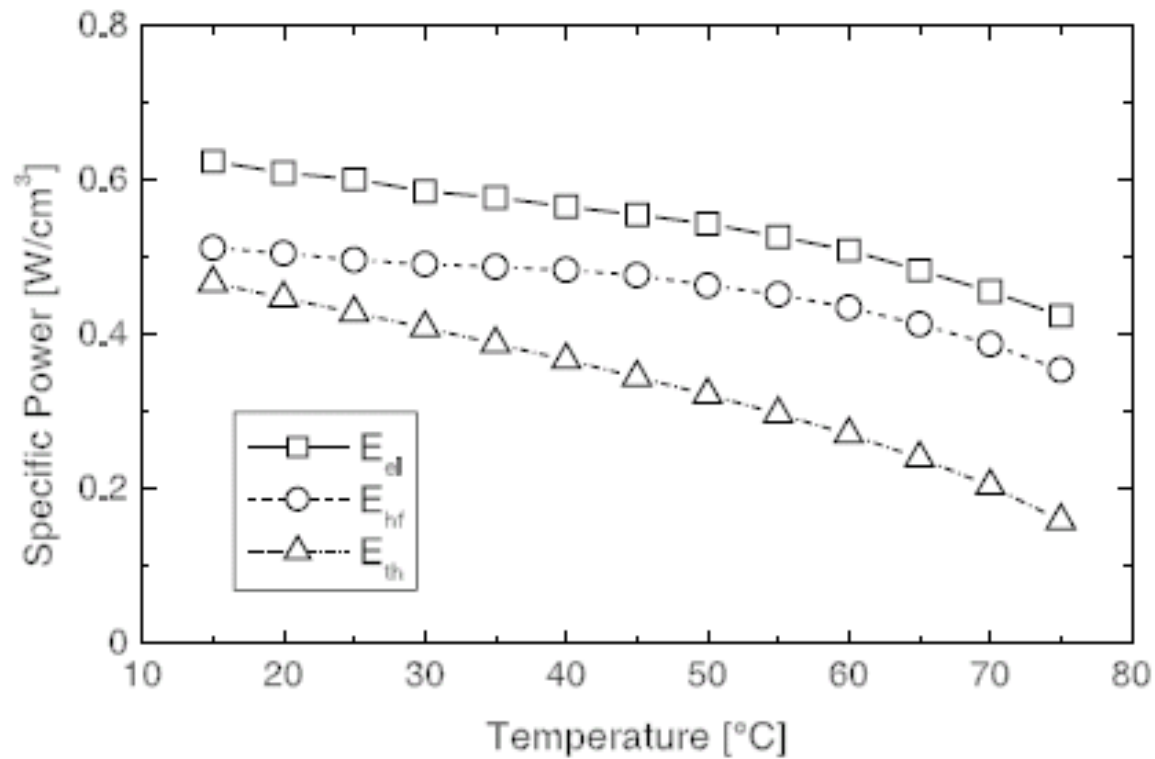
$\varepsilon = 500000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$



Porphyrin Decomposition

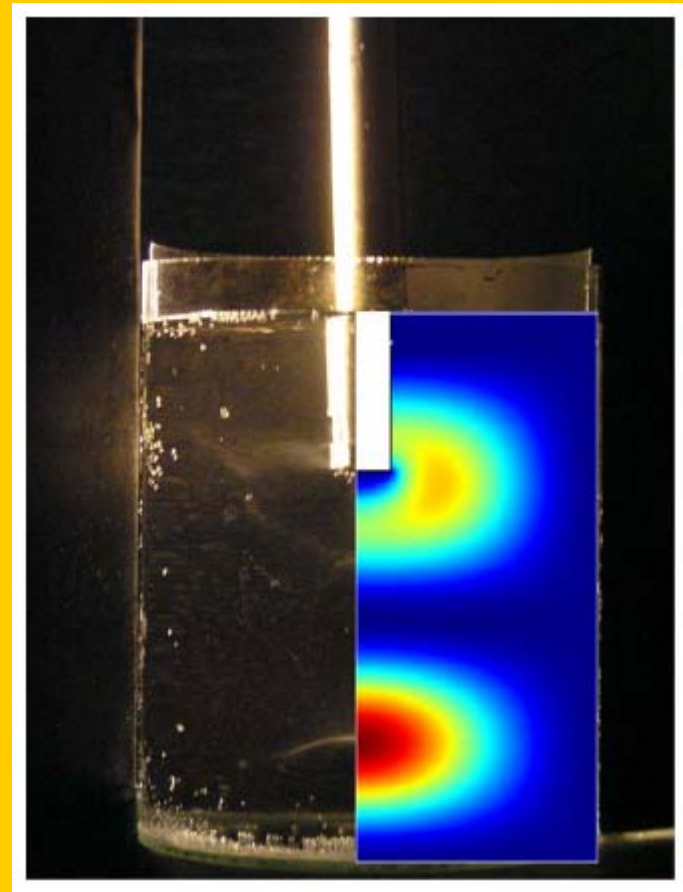
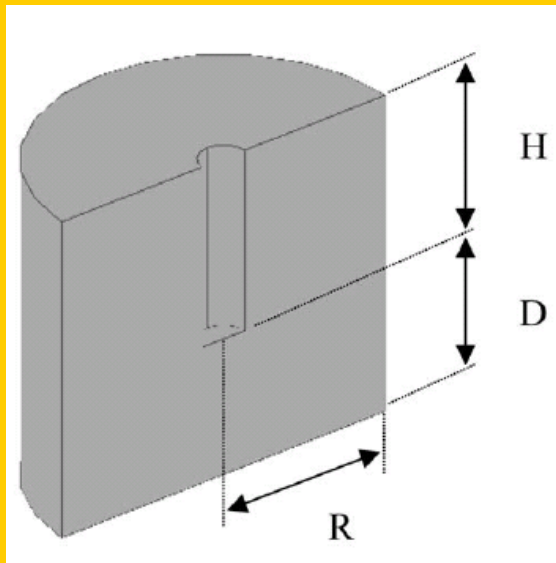


Power Measurement in Sonochemistry



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

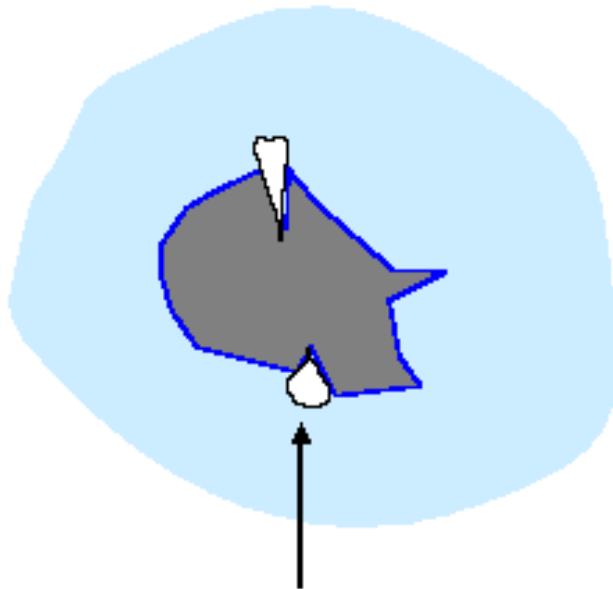
removal of unreactive coatings (oxides, nitrides, carbonaceous)

fragmentation of brittle materials, increased surface area



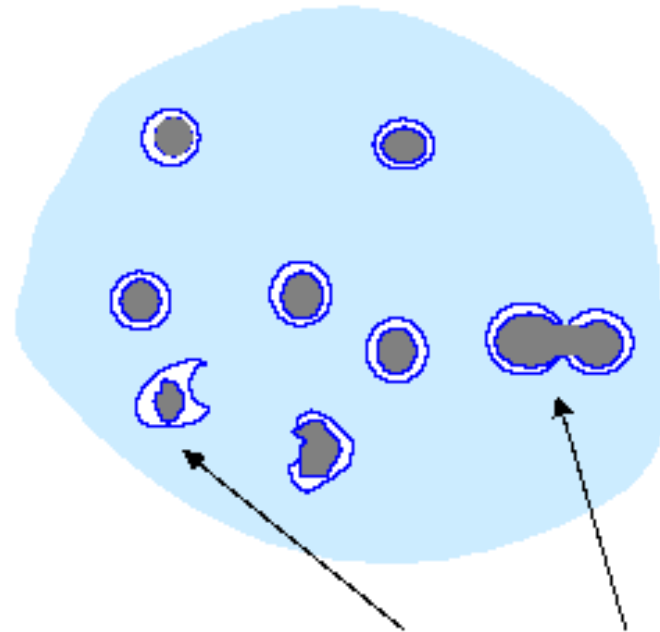
Heterogeneous Sonochemistry

LARGE PARTICLES



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

SMALL PARTICLES



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)**



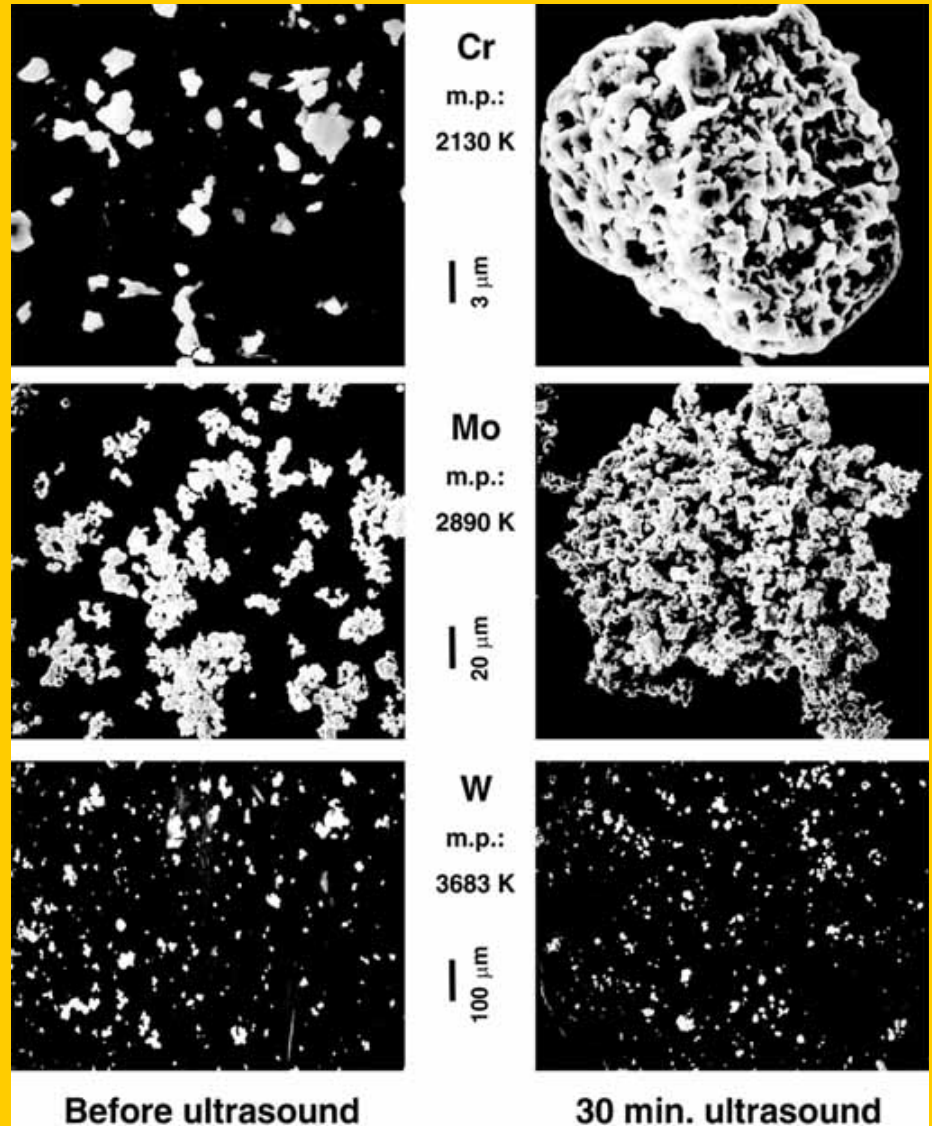
Heterogeneous Sonochemistry

Metal powders

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

W (mp 3683 K) does not

temperatures at the point of impact $\sim 3000\text{ }^{\circ}\text{C}$



Cavitation Corrosion of the Tip



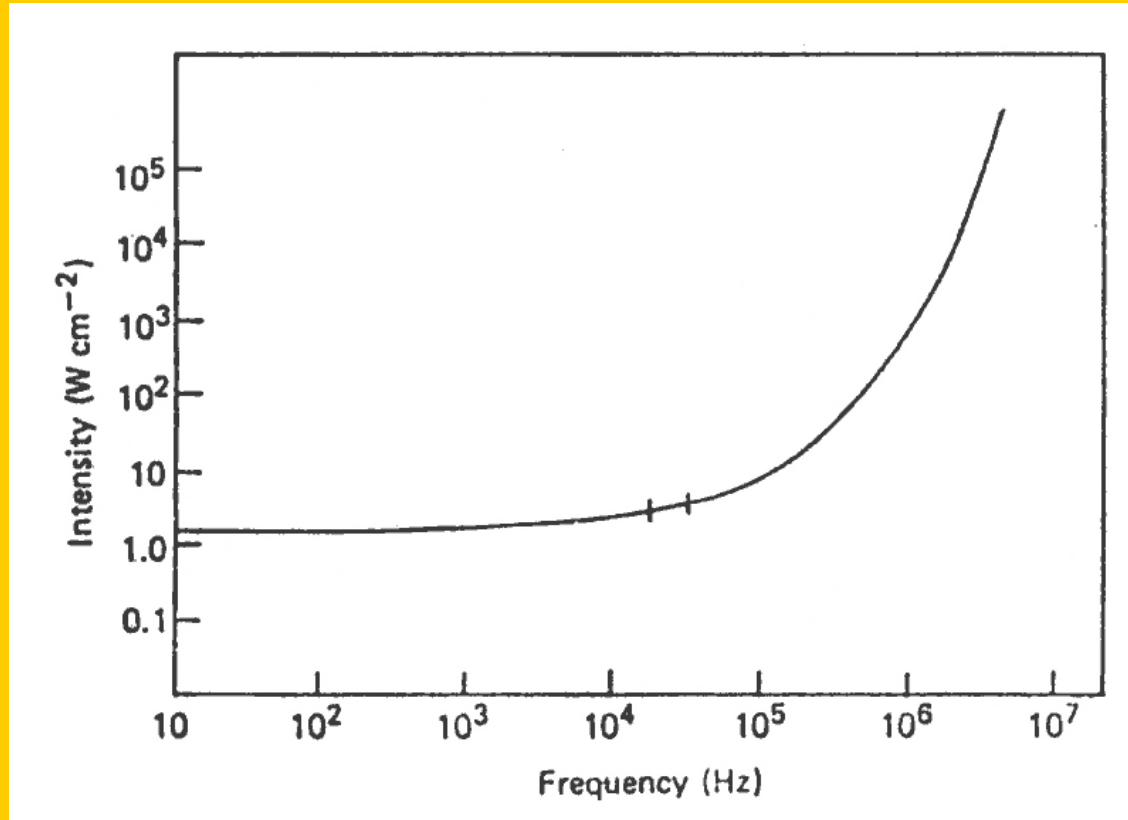
Control of Sonochemical Reactions

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, $10 - 100 \text{ W cm}^{-2}$

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 $^{\circ}\text{C}$, easy bubble formation, more reactant vapors inside bubbles, but the cavitation is cushioned



nonvolatile reactants - reaction in the thin layer (200 nm) surrounding the bubble, 2000 $^{\circ}\text{C}$, 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:

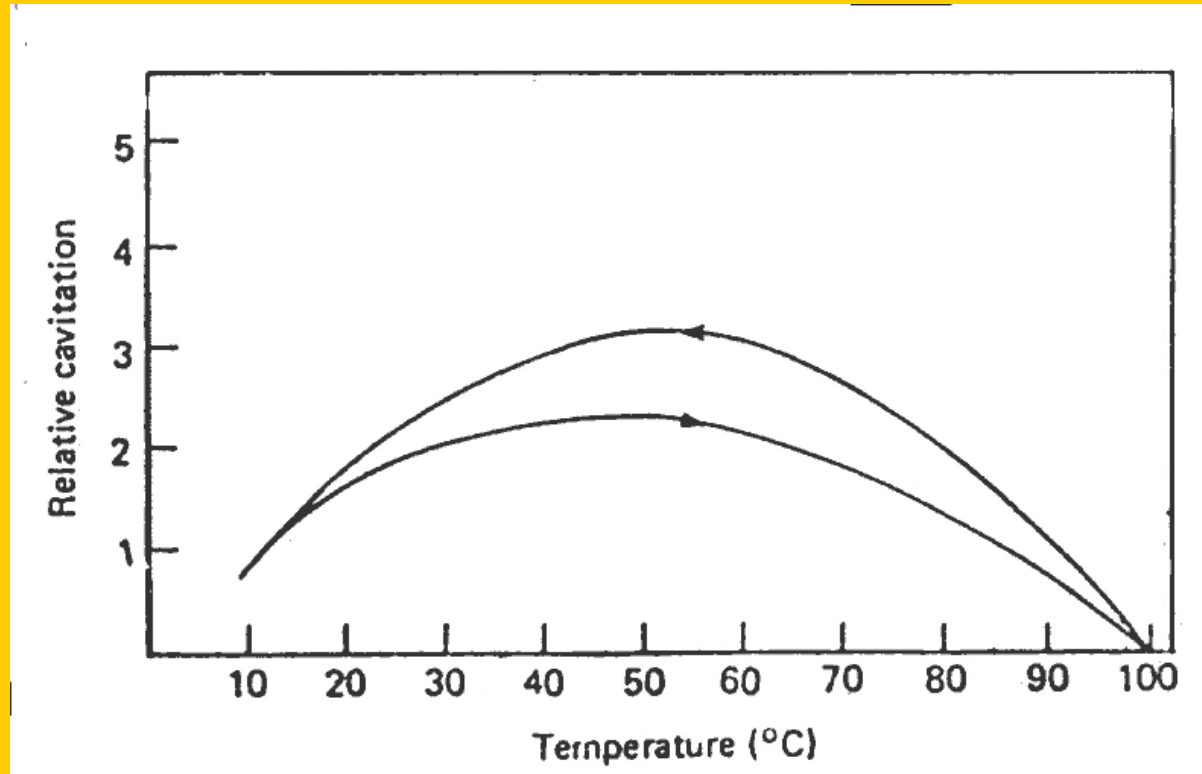
monoatomic (Ar) > diatomic (N₂) > triatomic (CO₂)

Xe: low thermal conductivity, heat of the collapsing cavity retained

He: high thermal conductivity, heat of the collapsing cavity dissipated, 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



monomodal MW distribution

Homogeneous Sonochemical Reactions

Liquids = heating/cooling by cavity implosions



precursor decomposition:



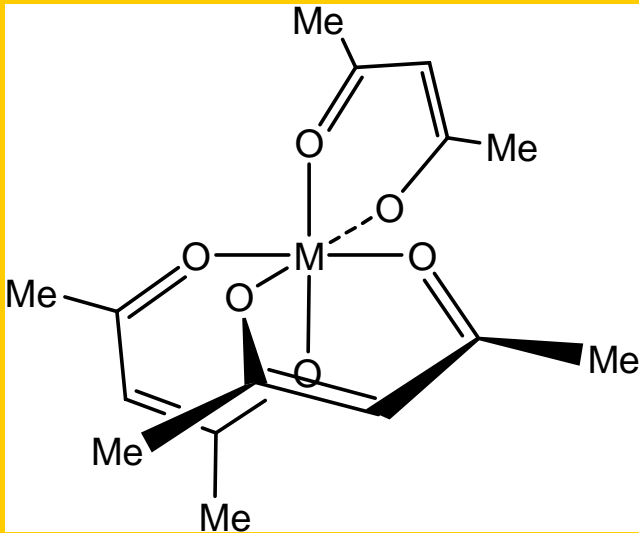
nitrides, carbides, sulfides

alkane cracking

polymer degradation, lower MW, surface modification

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

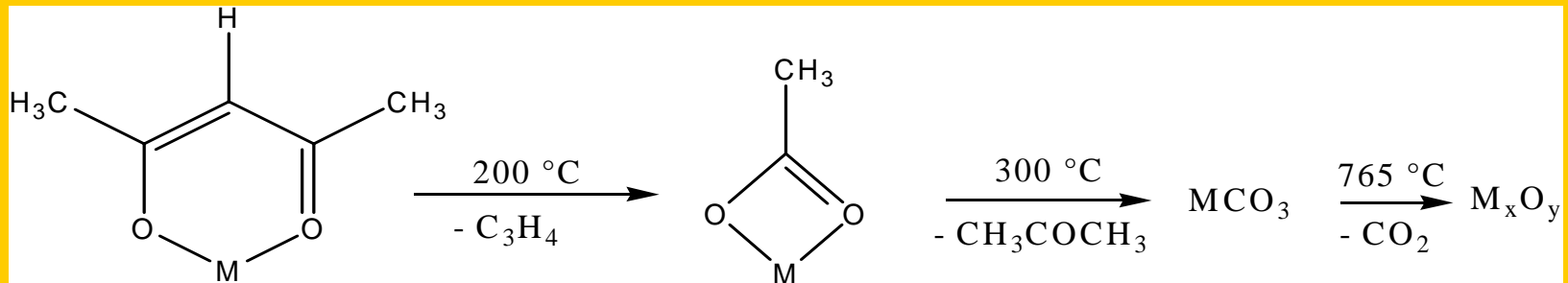
$M(\text{acac})_n$ as Precursors



- 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

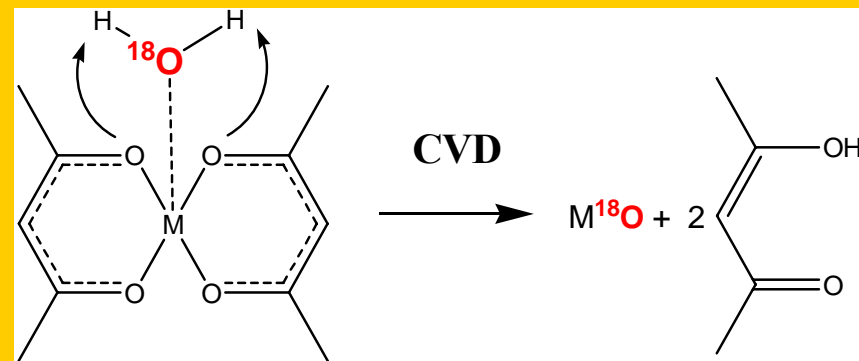
Chemistry of $M(\text{acac})_n$ Precursors

Thermal decomposition pathway



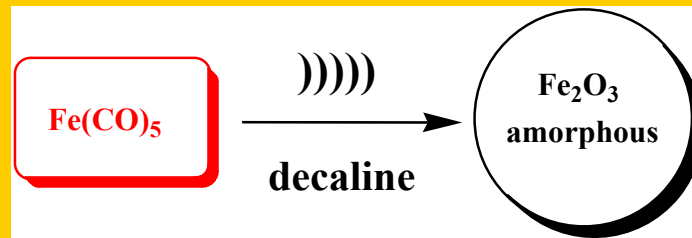
Ismail, H. M. *J. Anal. Appl. Pyrolysis* 1991, 21, 315–326.

Ligand Removal by Water



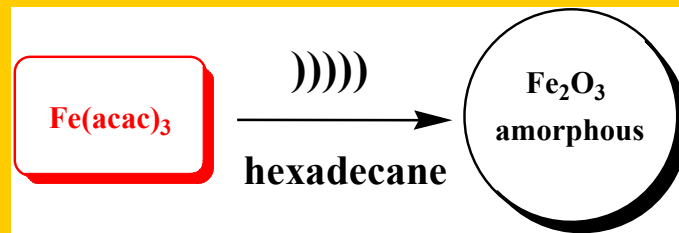
Pinkas, J.; Huffman, J. C.; Baxter, D. V.; Chisholm, M. H.; Caulton, K. G. *Chem. Mater.* 1995, 7, 1589–1596.

Sonochemical Synthesis of Iron Oxide Nanoparticles



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

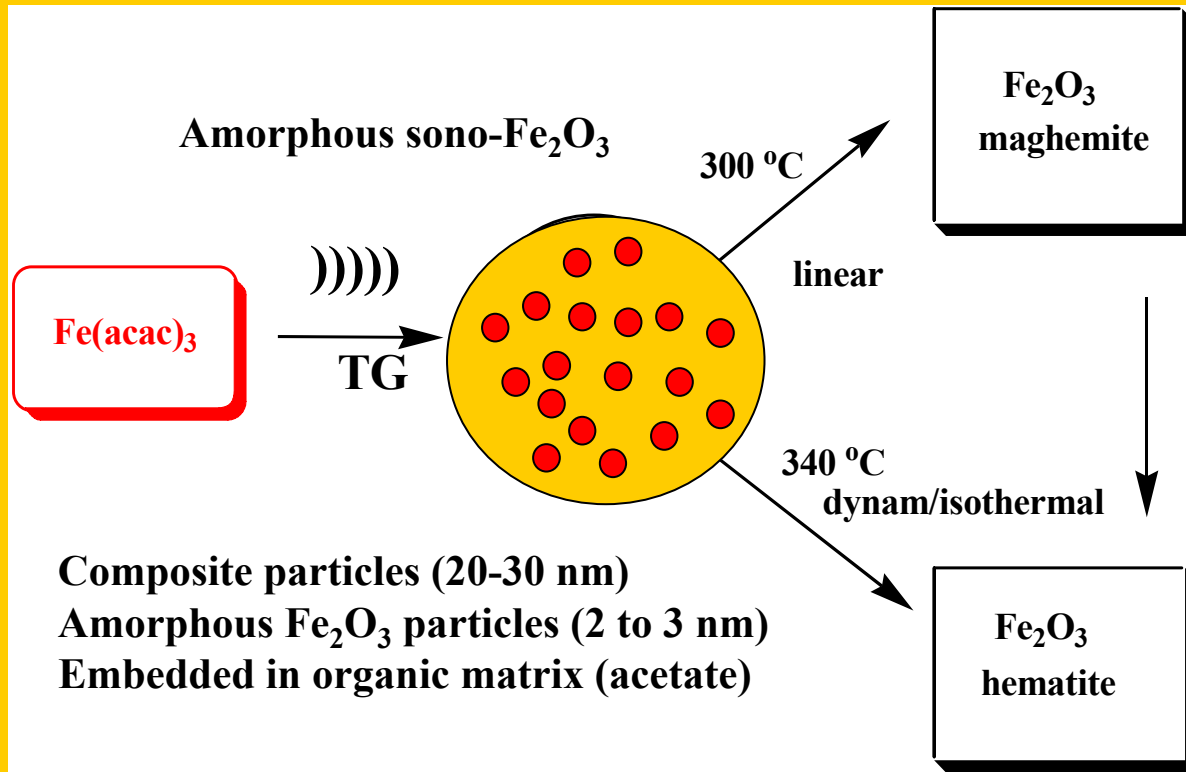
Cao, X.; Koltypin, Yu.; Prozorov, R.; Katabya, G.; Gedanken, A.
J. Mater. Chem. 1997, 7, 2447–2451.



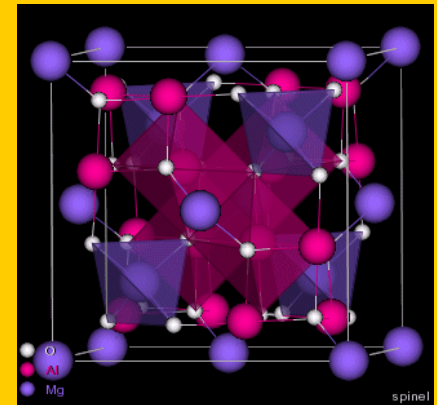
Amorphous product, by heating to 700 °C converted to α -Fe₂O₃ 20–40 nm

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

Sonochemical Synthesis of Iron Oxide Nanoparticles



Defect spinel

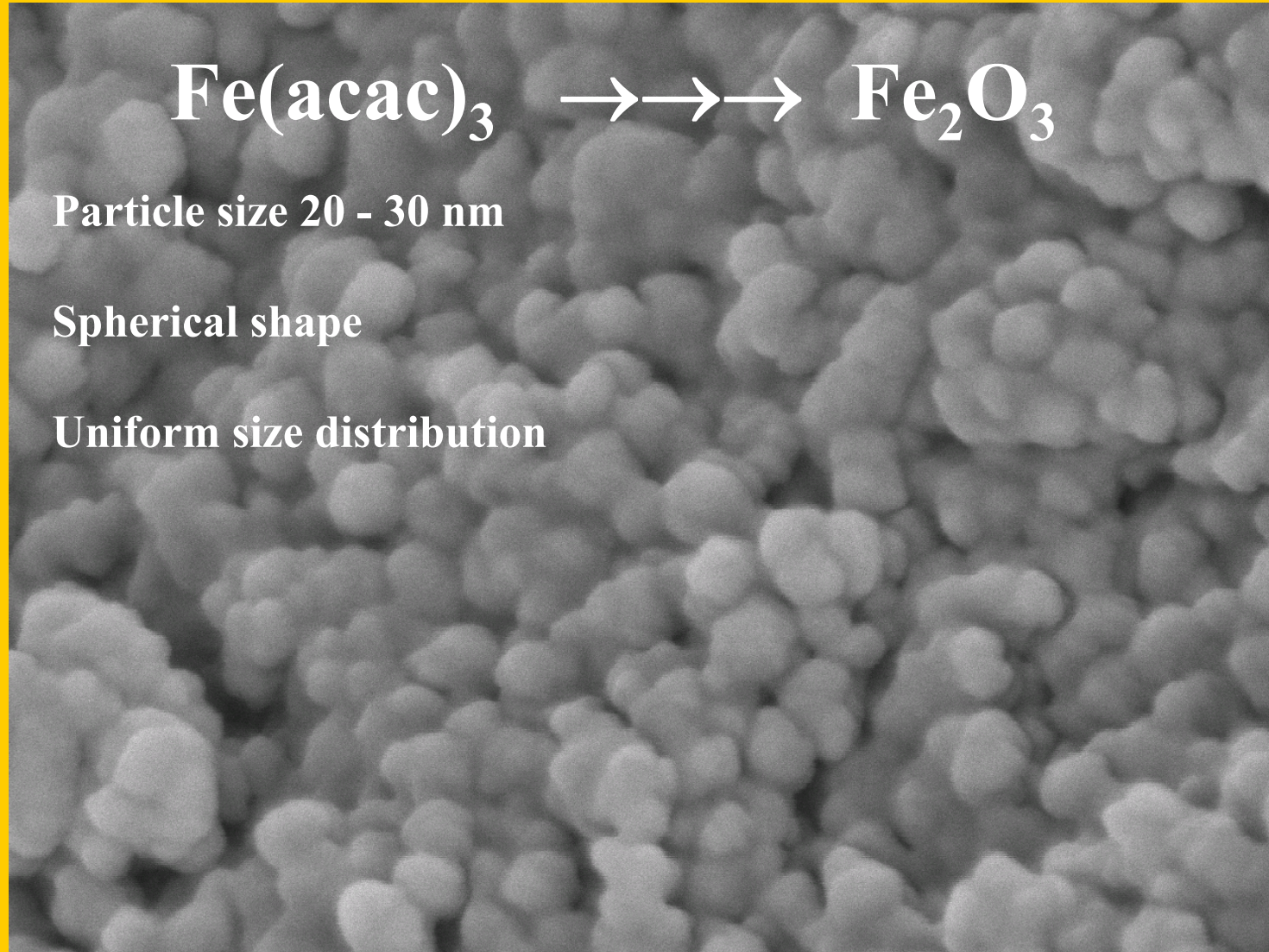


Corundum



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

SEM of Nanoscopic Fe_2O_3



Particle size 20 - 30 nm

Spherical shape

Uniform size distribution

ISI

SEI

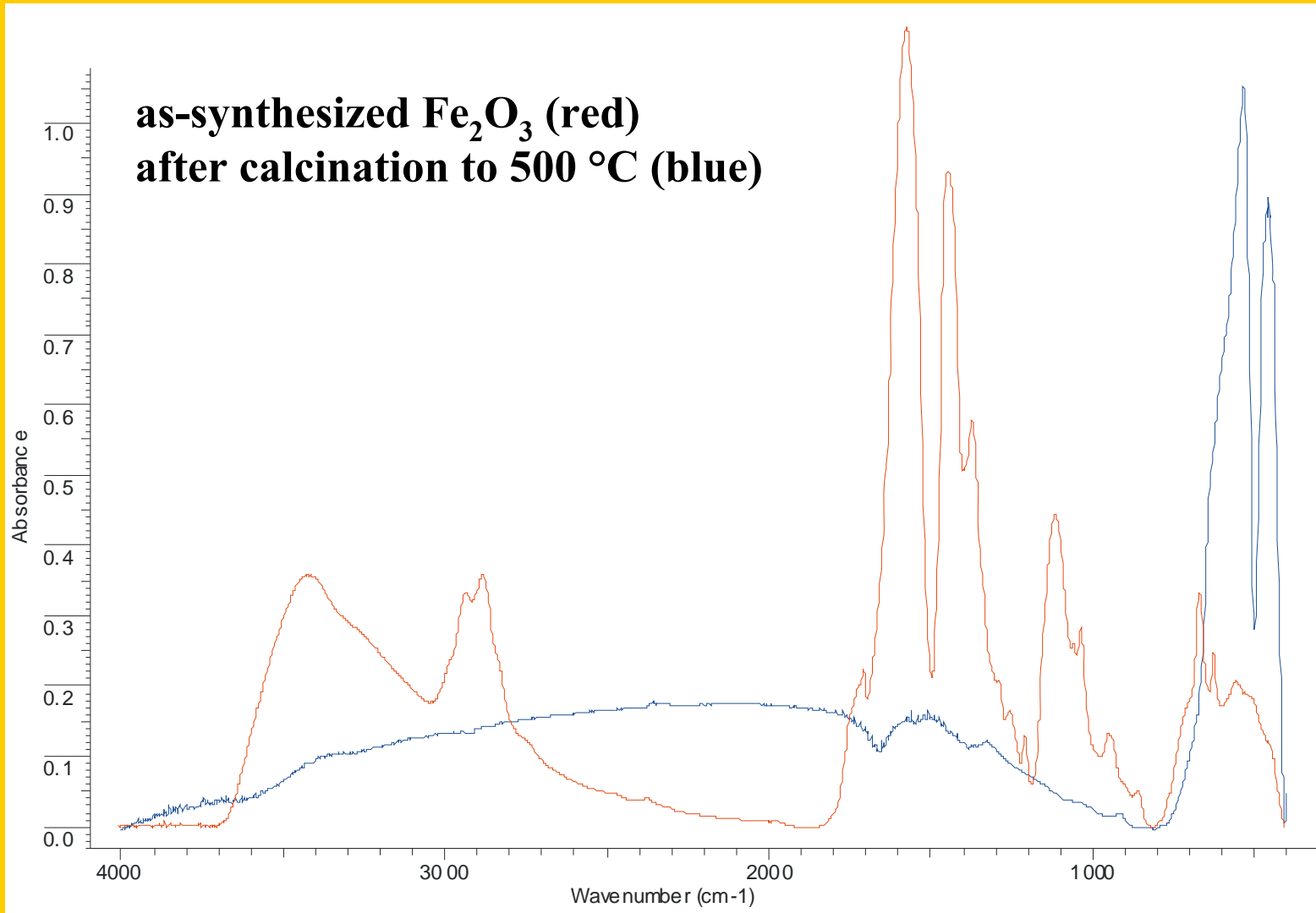
5.0kV

X150,000

100nm

WD 3.0mm

IR Spectrum of Sono-Fe₂O₃



IR Spectrum of Sono-Fe₂O₃

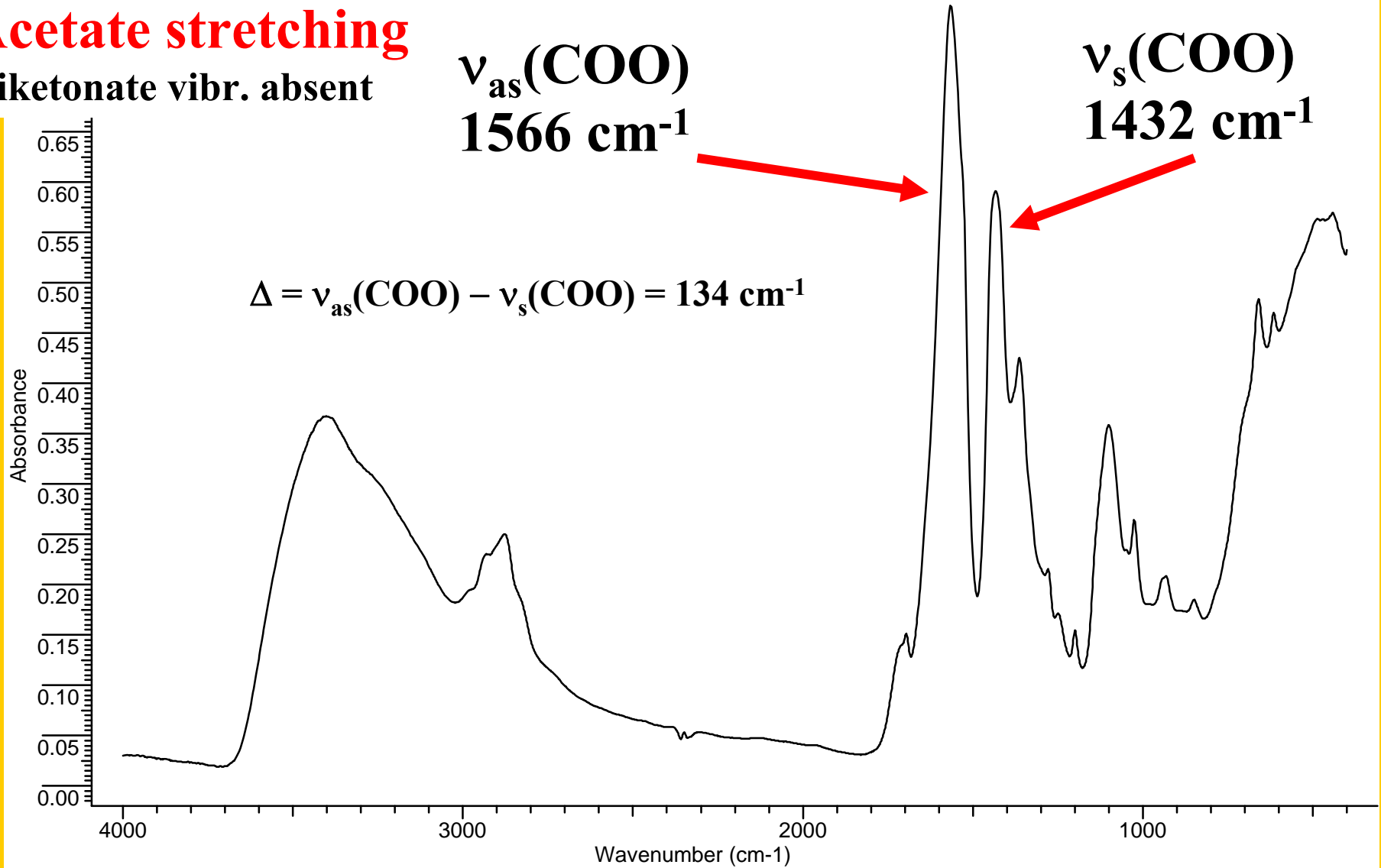
Acetate stretching

Diketonate vibr. absent

$\nu_{as}(\text{COO})$
1566 cm⁻¹

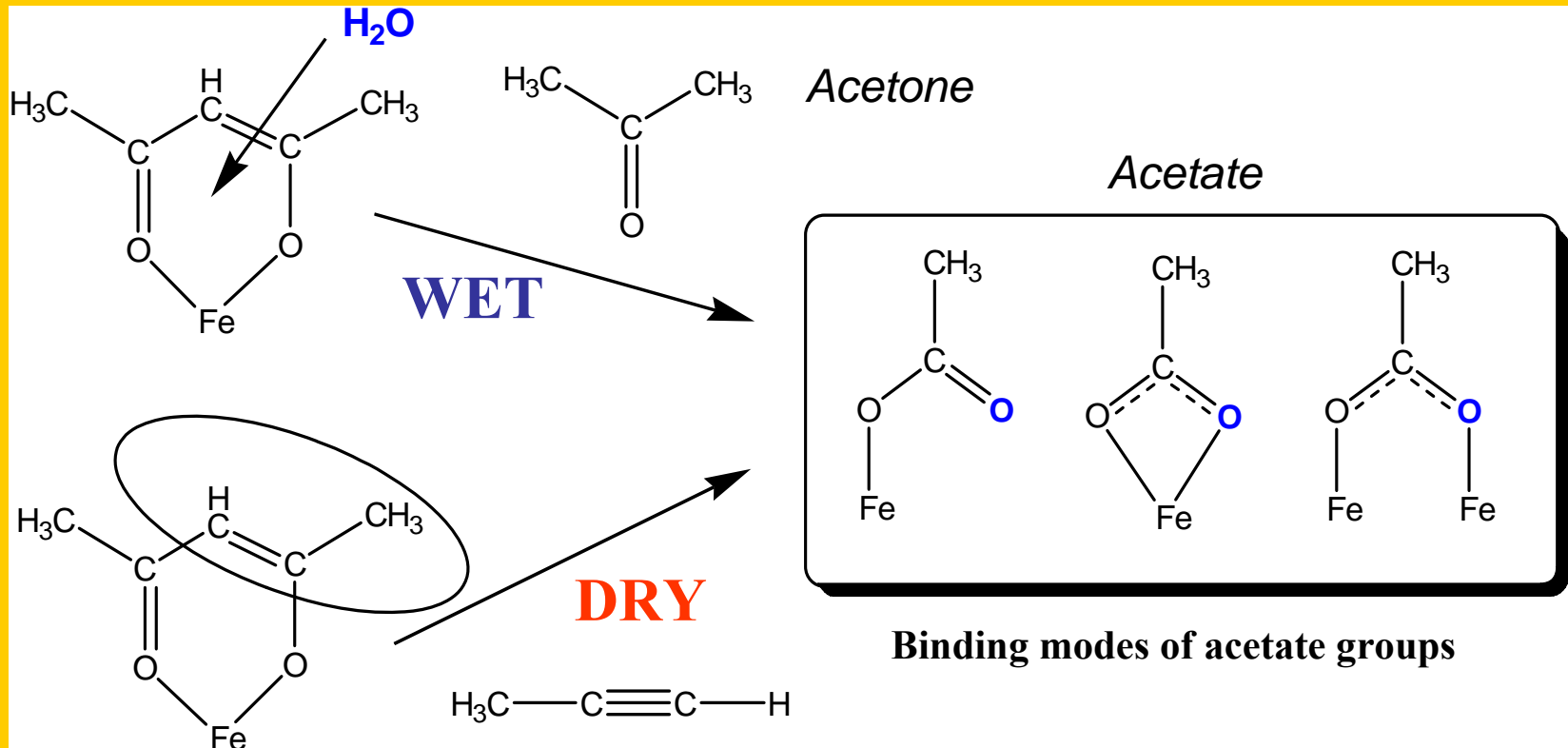
$\nu_s(\text{COO})$
1432 cm⁻¹

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



Decomposition of Acac Ligands

Speculation about the nature of residual organic groups



Deacon-Phillips Rules

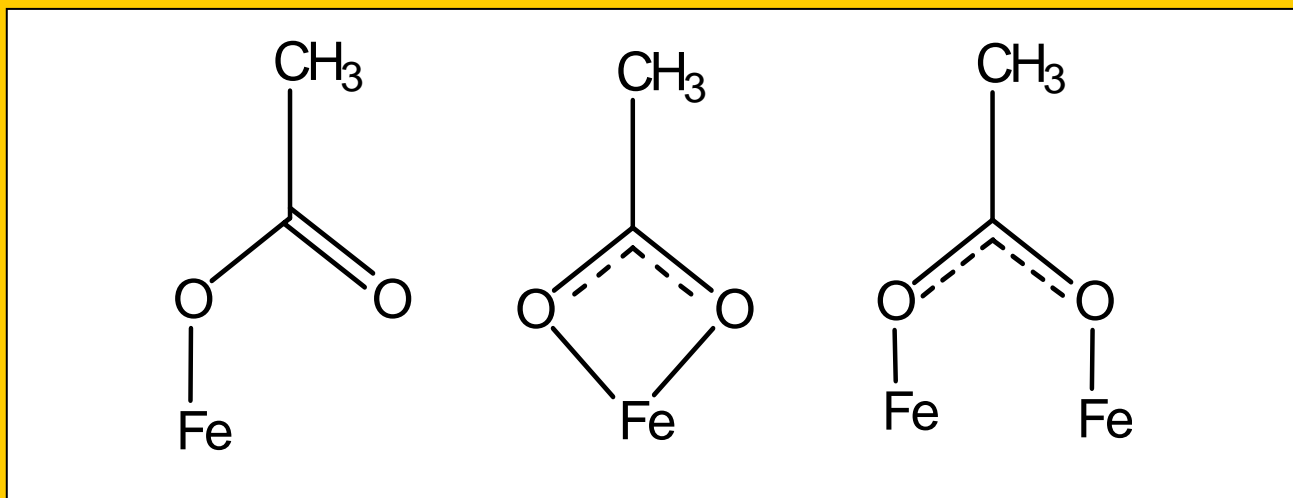
$$\Delta = \nu_{as}(\text{COO}) - \nu_s(\text{COO})$$

$$\Delta \text{CH}_3\text{COO}^- = 164 \text{ cm}^{-1}$$

Δ larger than ionic form = unidentate

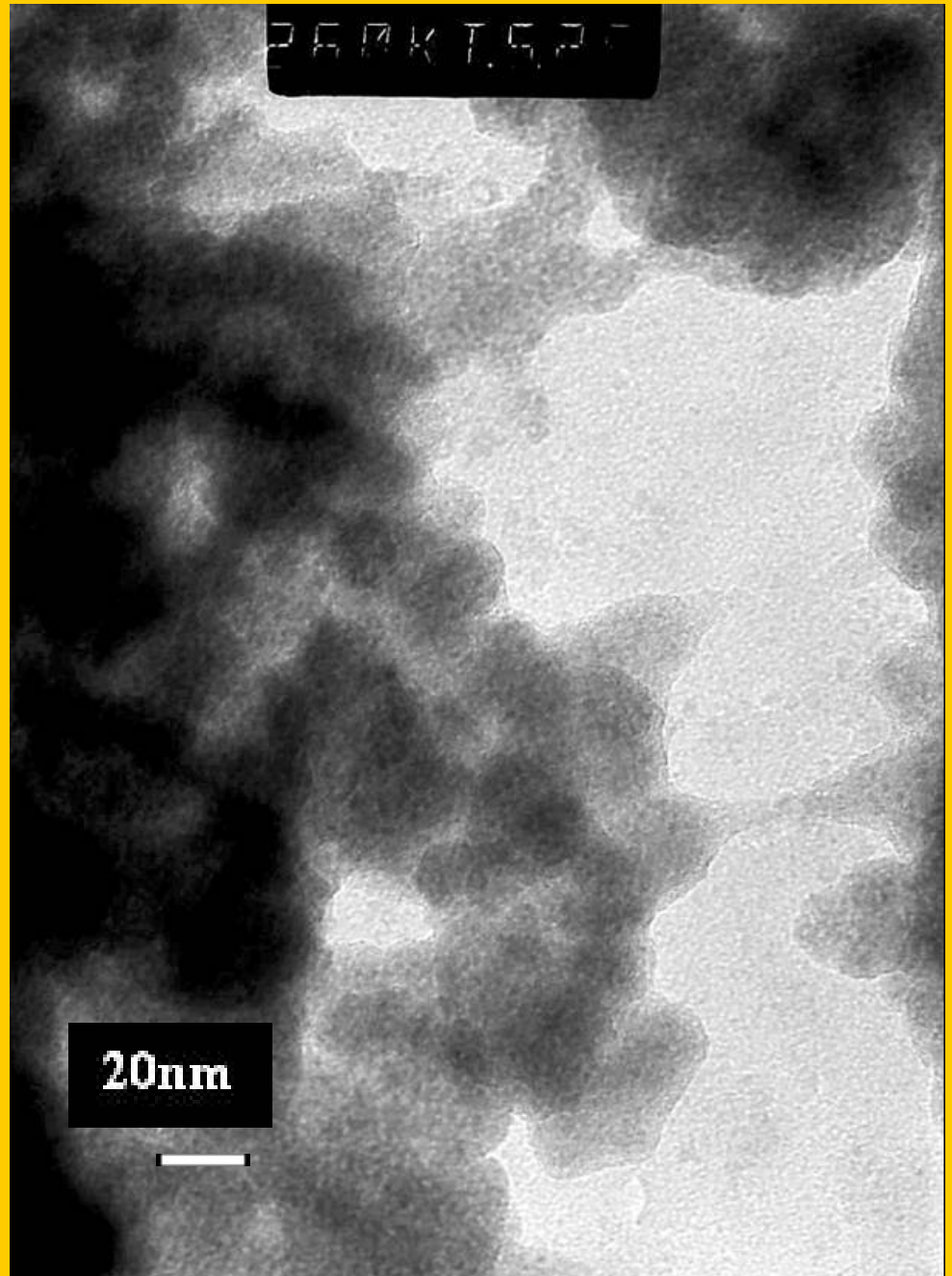
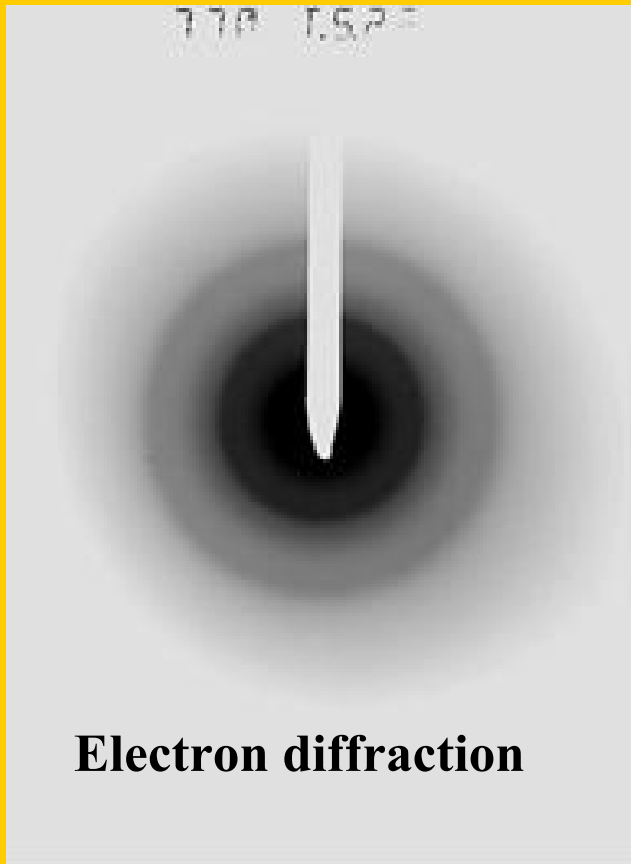
Δ smaller than ionic form = bidentate

Δ comparable to ionic form = bridging

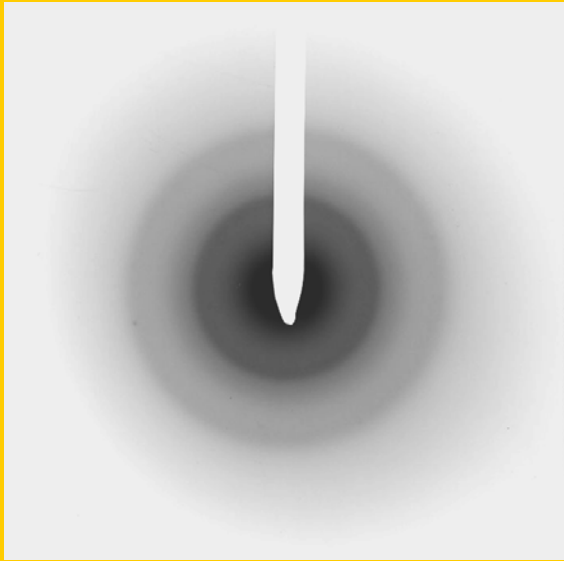


TEM

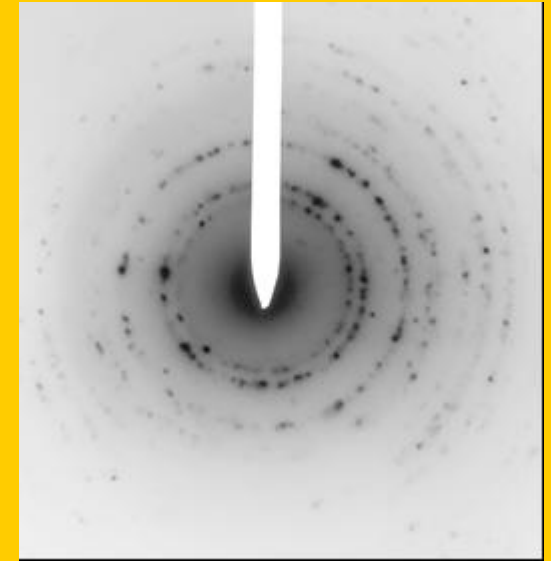
proves amorphous
character
of sono- Fe_2O_3



Crystallization of Amorphous Fe_2O_3 under TEM Beam



Electron diffraction



Maghemite or Magnetite



Time under TEM beam

Amorphous Fe_2O_3

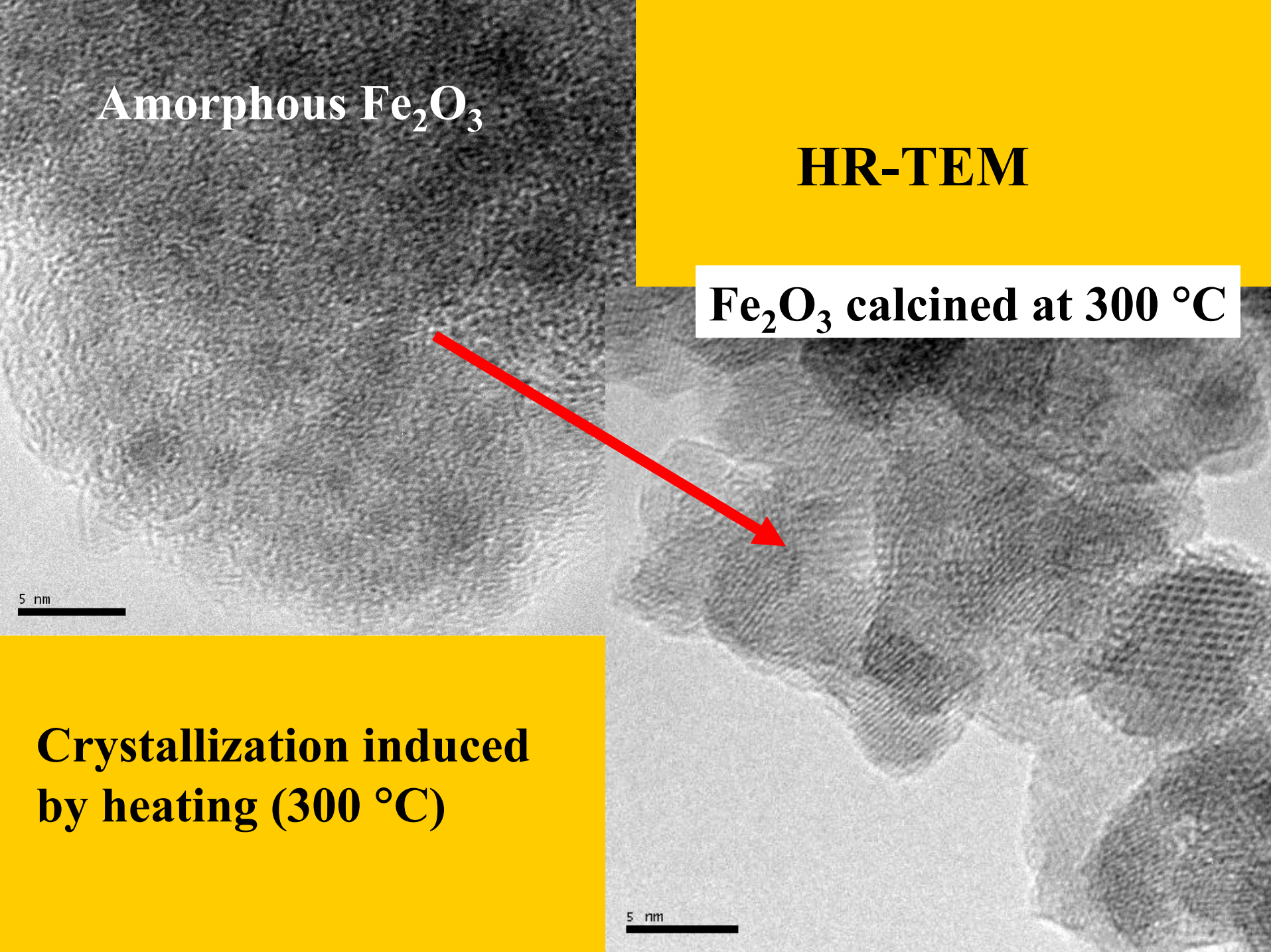
HR-TEM

Fe_2O_3 calcined at 300 °C

**Crystallization induced
by heating (300 °C)**

5 nm

5 nm



TEM of amorphous Fe_2O_3

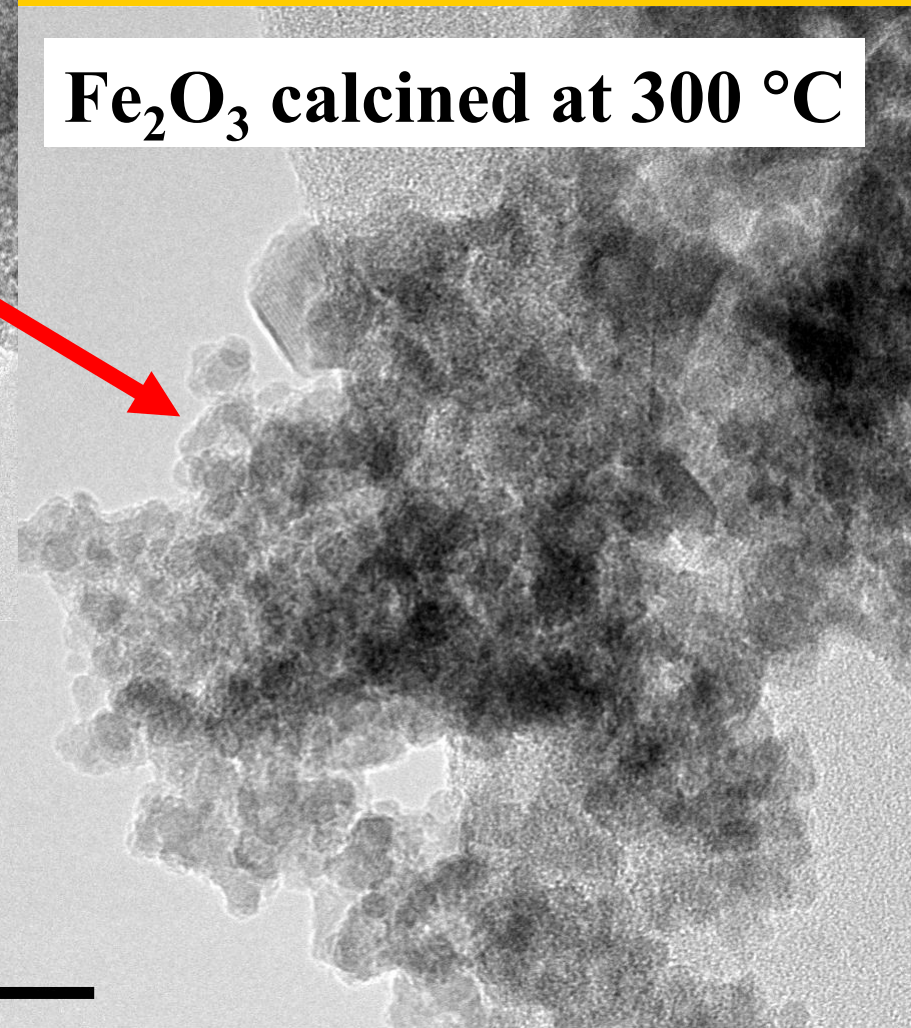
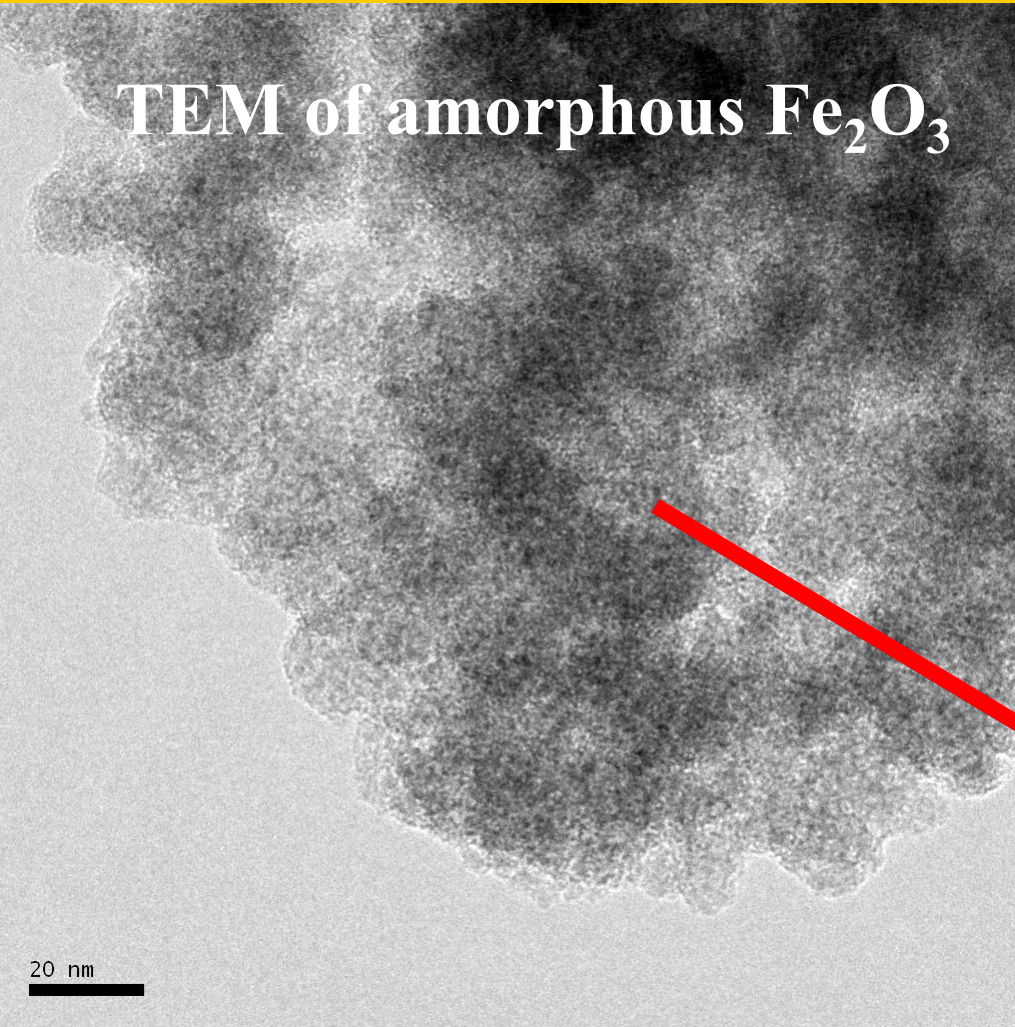
TEM

Fe_2O_3 calcined at 300 °C

20 nm

20 nm

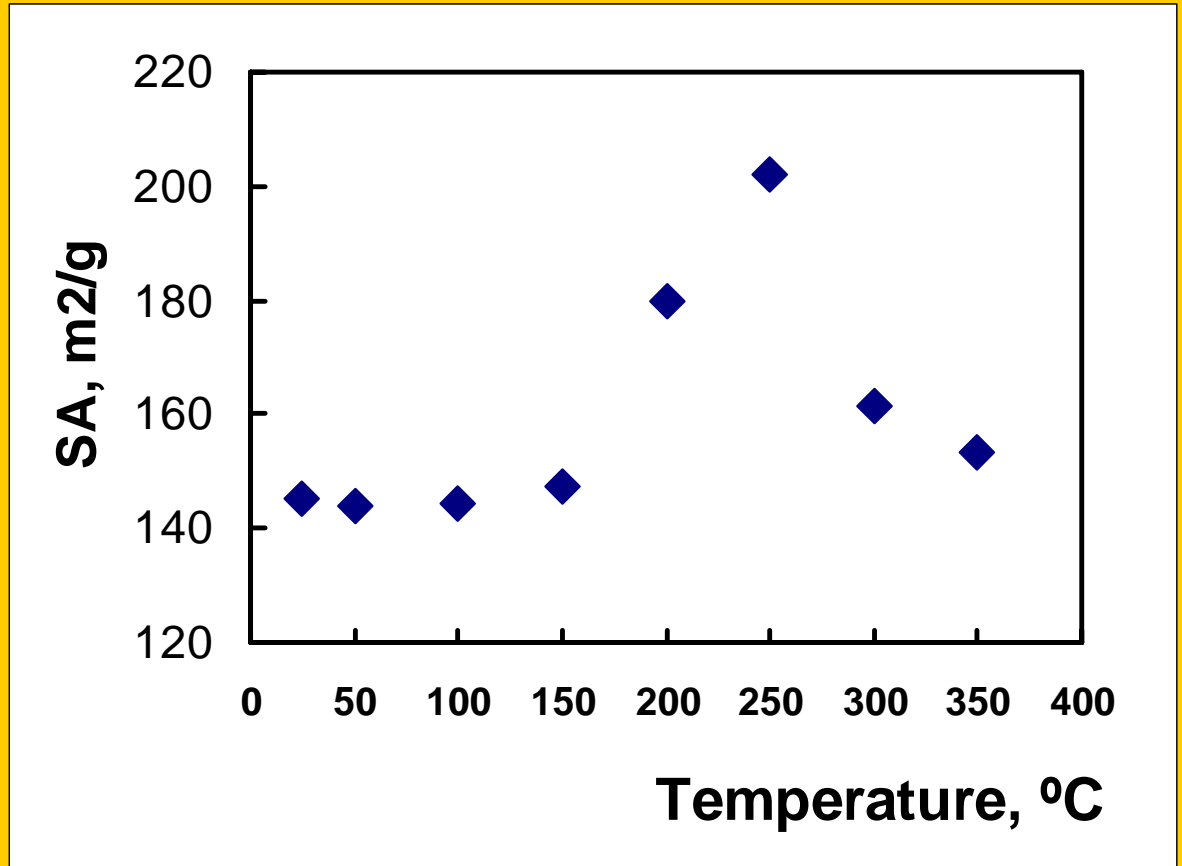
**Smaller particle size
on calcination – why?**



Specific Surface Area

Surface area 48 to 260 m² g⁻¹ (BET) depending on H₂O content

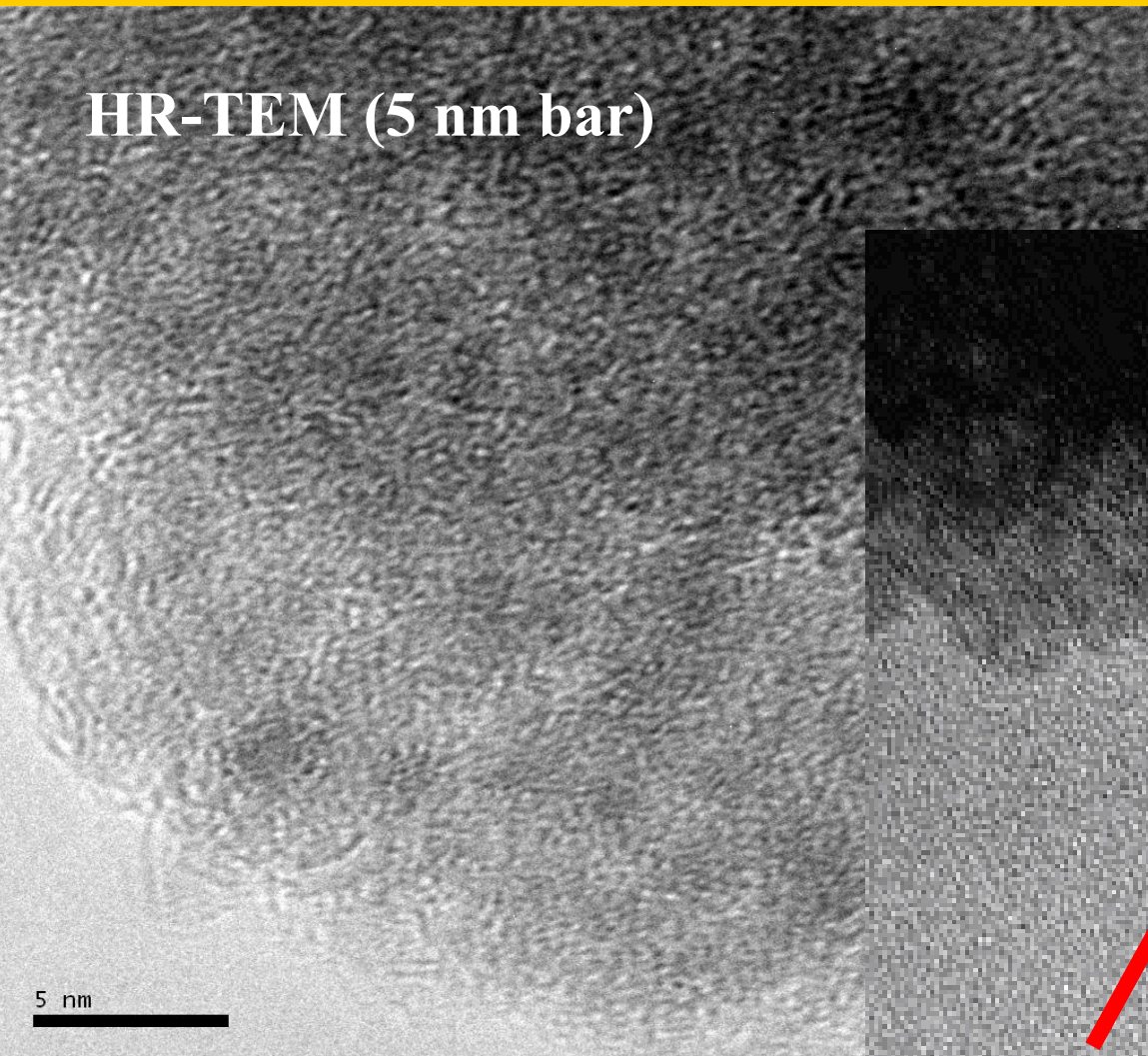
BET surface area of the Fe₂O₃ heated to different temperatures during 12h outgassing periods



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

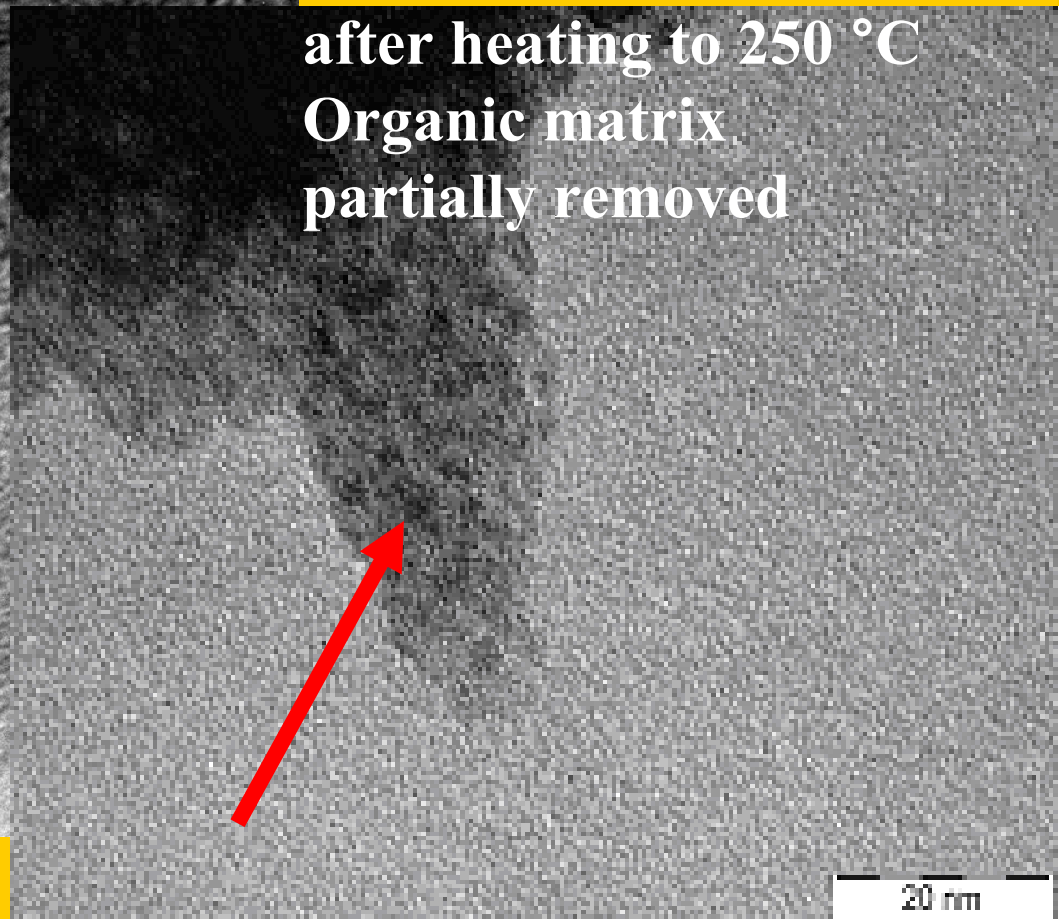
Composite Particles of Sono-Fe₂O₃

HR-TEM (5 nm bar)



TEM (20 nm bar)

after heating to 250 °C
Organic matrix
partially removed



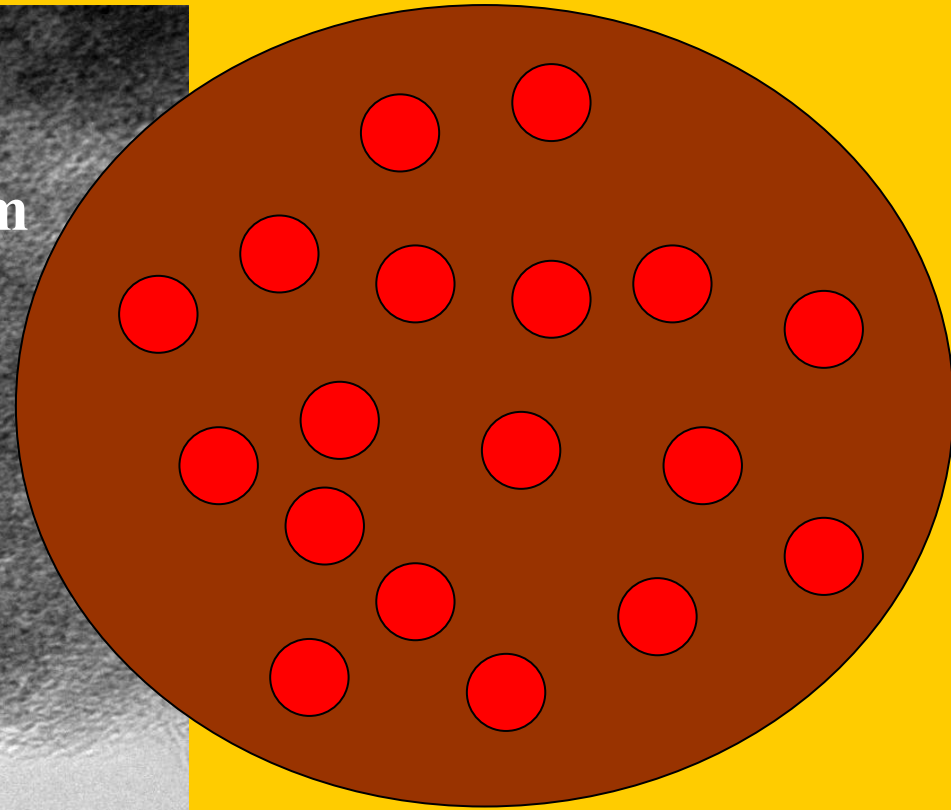
Composite Particles of Fe_2O_3

TEM (10 nm bar)

Iron oxide particle size 2 to 3 nm

Embedded in organic matrix

10 nm



XRD

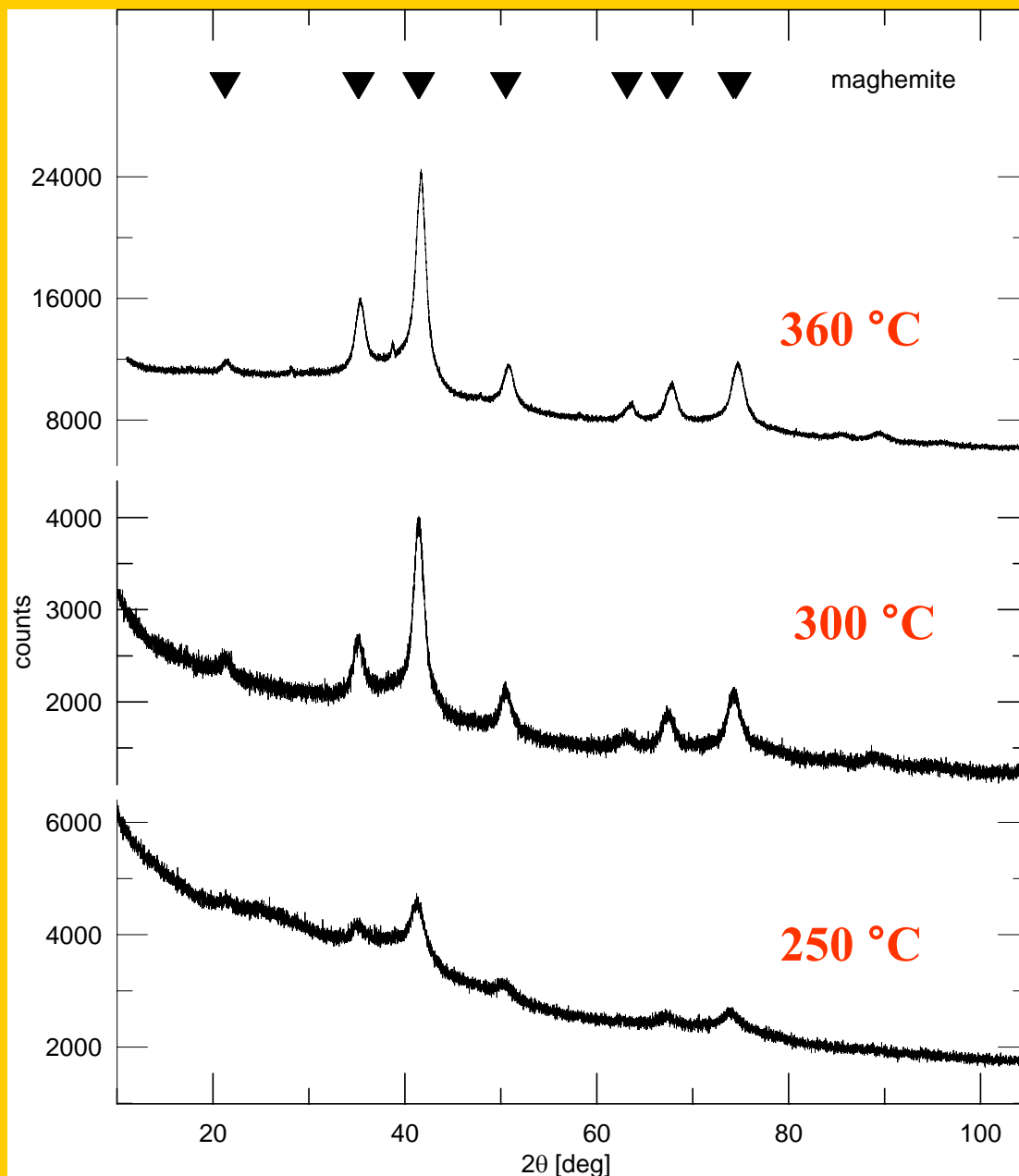
of amorphous Fe_2O_3

heated dynamically in air

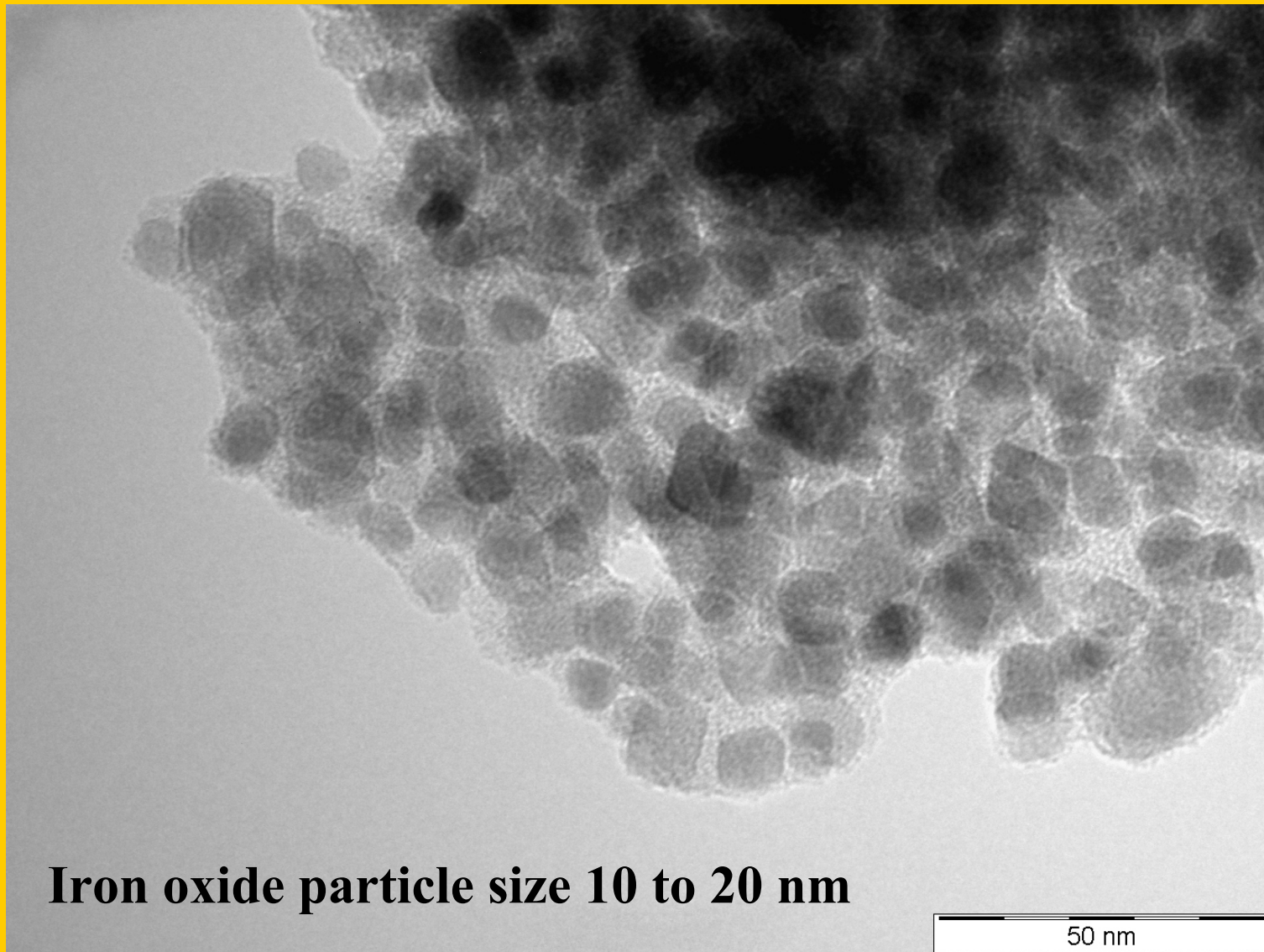
up to 250, 300, and 360 °C

Maghemite

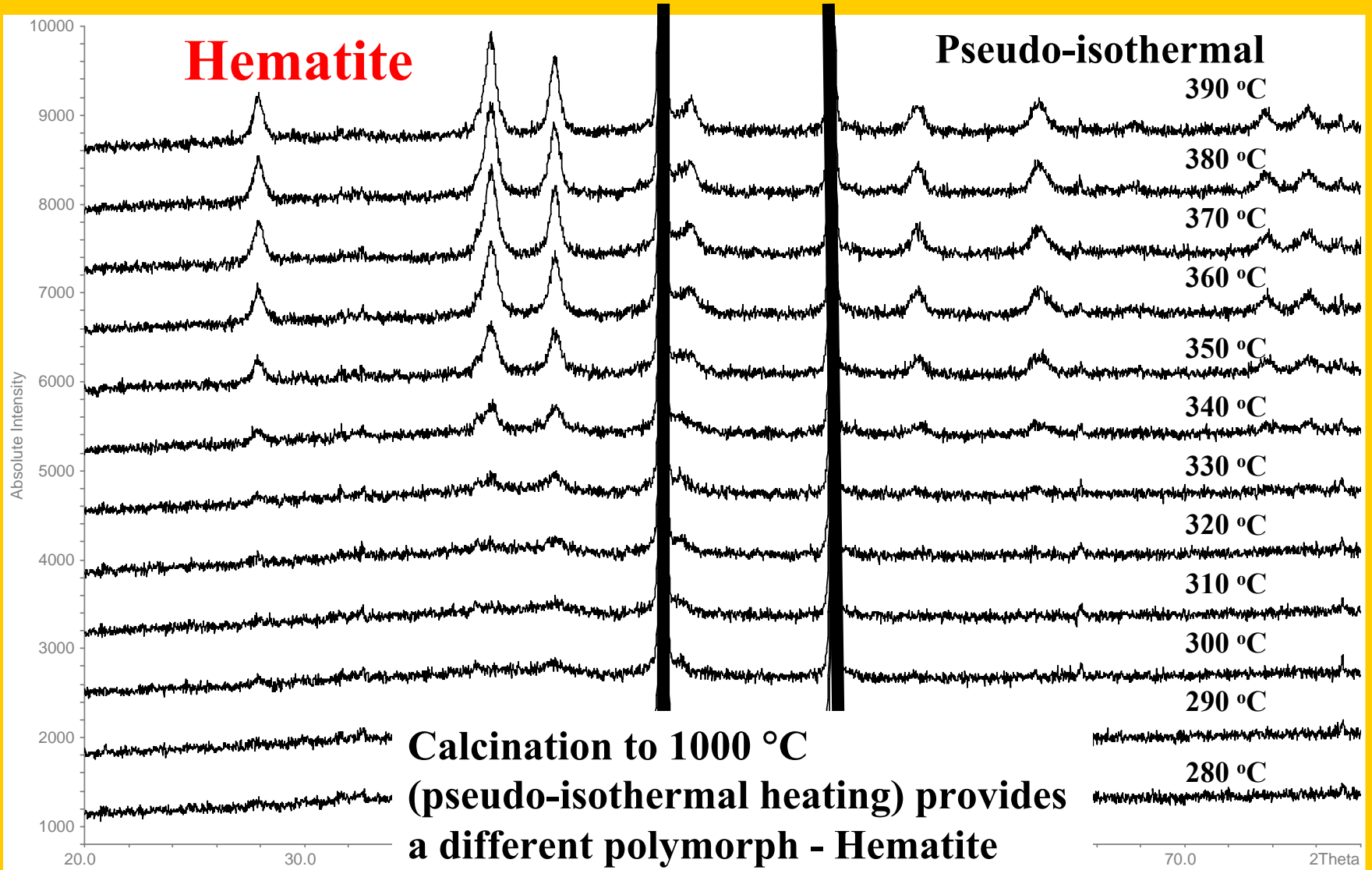
$\gamma - \text{Fe}_2\text{O}_3$



TEM of Fe_2O_3 Calcined at 600 °C



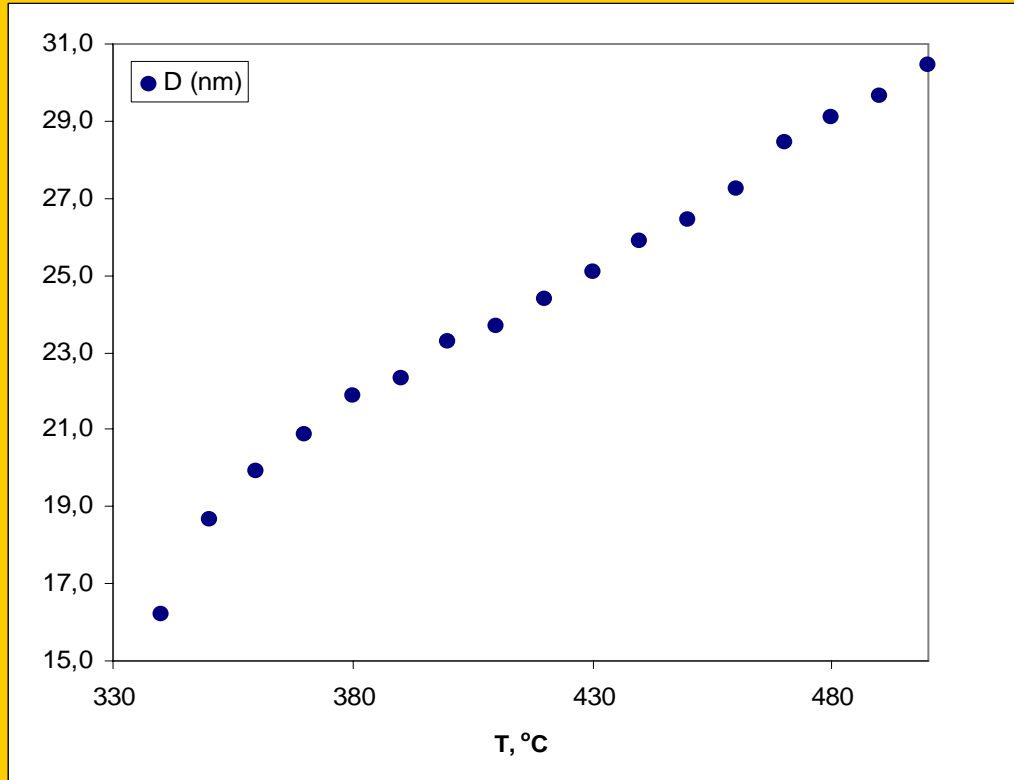
HT-XRD of Sono-Fe₂O₃ 280 - 390 °C



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