

# Diagnostics des plasmas produits par ablation laser à une interface liquide-solide.

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@ Fête des Lumières

Interest of laser ablation in liquids

Characteristic time scales in laser ablation

Shock waves

Plasma/liquid interaction and bubble formation

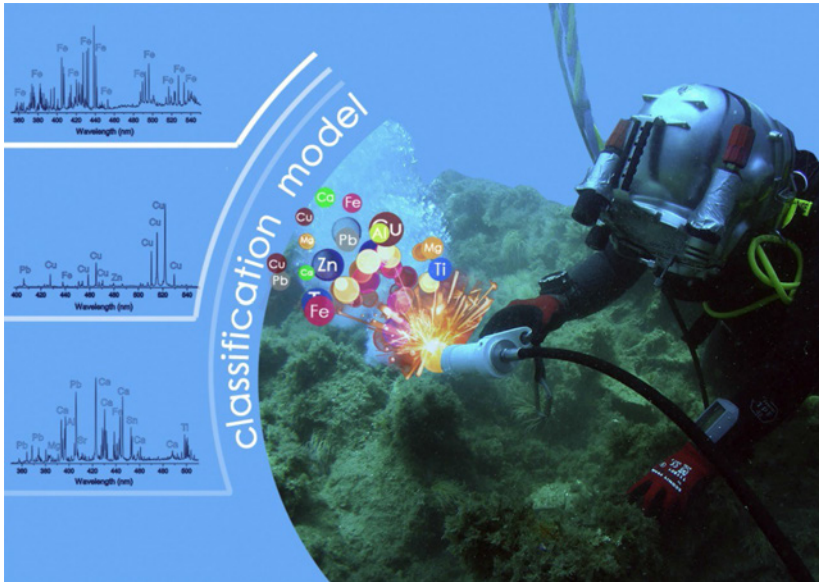
Plasma spectroscopy

Bubble dynamics



time

## LIBS underwater

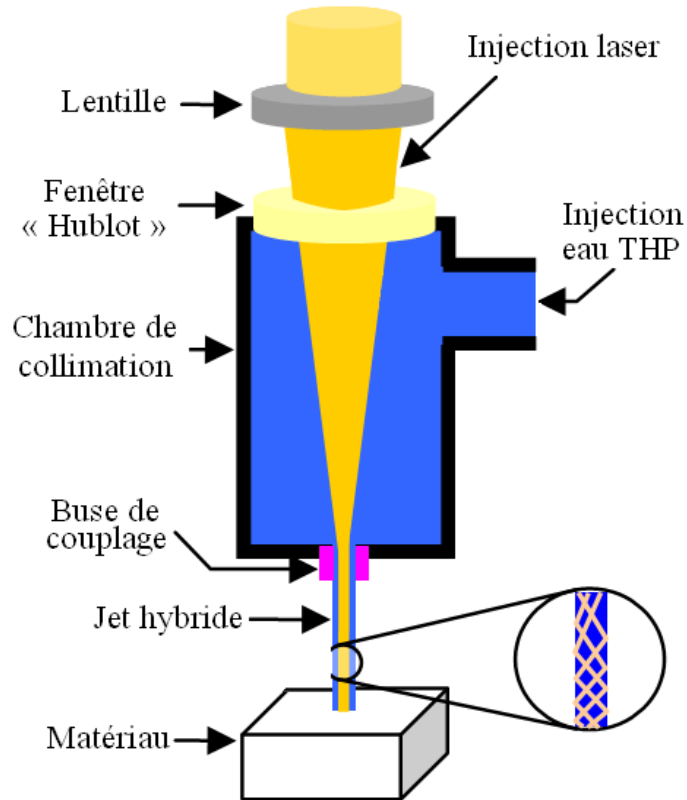


Interest: Geological exploration (oil industry)  
Recognition of archeological materials...

M. López-Claros et al., *J. Cultural Heritage* 29,  
75–81 (2018)



## Microfabrication



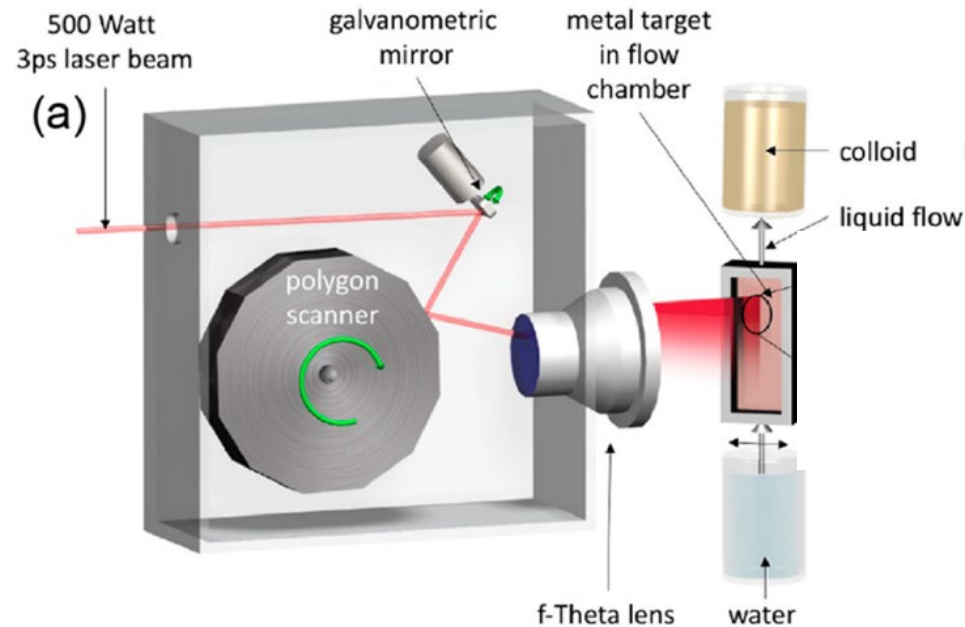
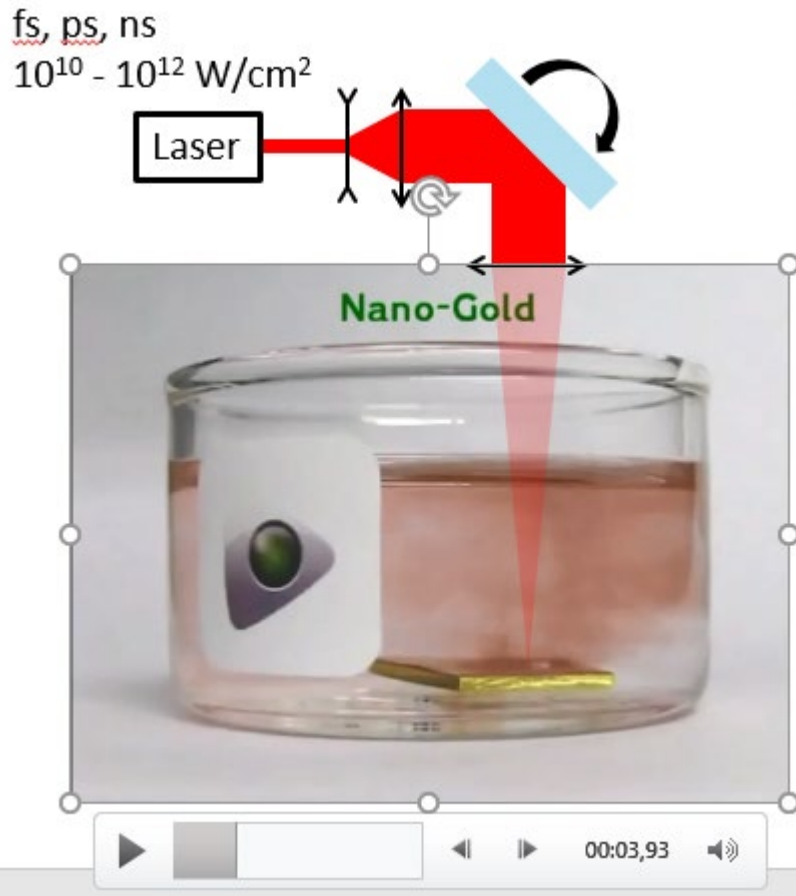
Thèse de Laurent Weiss, *Contribution au développement d'un procédé de découpe laser haute-énergie/ jet d'eau haute-pression couplés. Application à la découpe d'alliages métalliques.* Univ. Lorraine 5 juillet 2013

<https://www.sugino.com/site/water-jet-and-laser-machine-e/>



## Laser generation of colloids

Interest: one step process, particles with surface free of ligands, versatile...

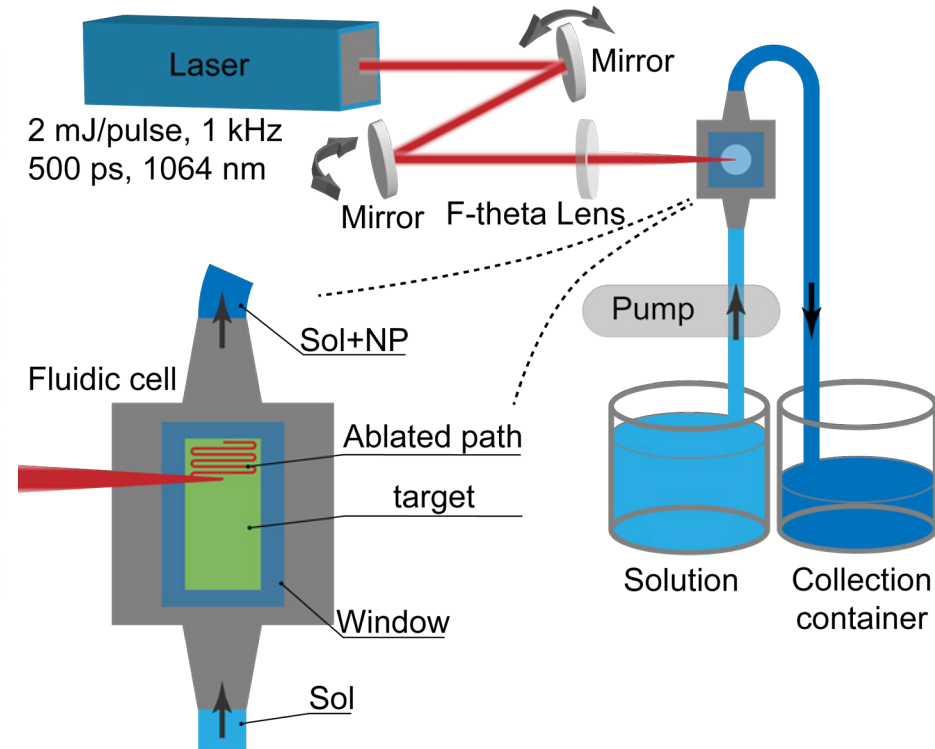


**Productivity > 1g/hour**  
**(Pt, Au, Ag, Al, Cu, Ti)**

R. Streubel *et al.*, *Opt. Lett.* **41**, 1486–1489 (2016).

R. Streubel *et al.*, *Nanotechnology* **27**, 205602 (2016).

## Continuous flow setup



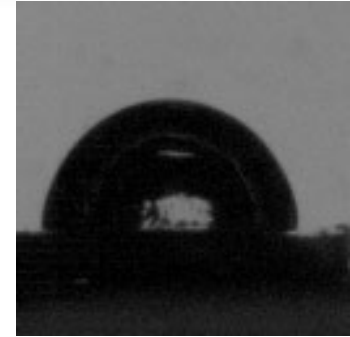
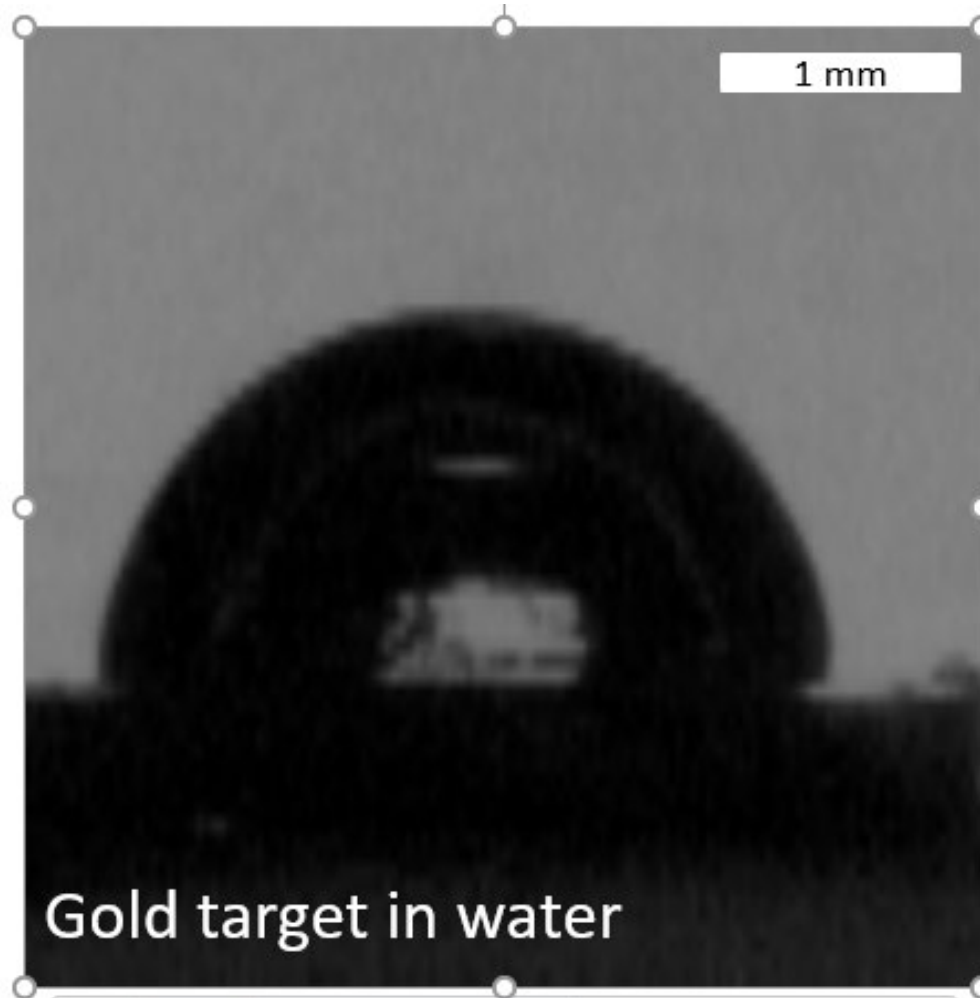
**Productivity 15 – 40 mg/hour**

# Characteristic time scales in laser ablation

- **Overview**
- **Molecular dynamics**

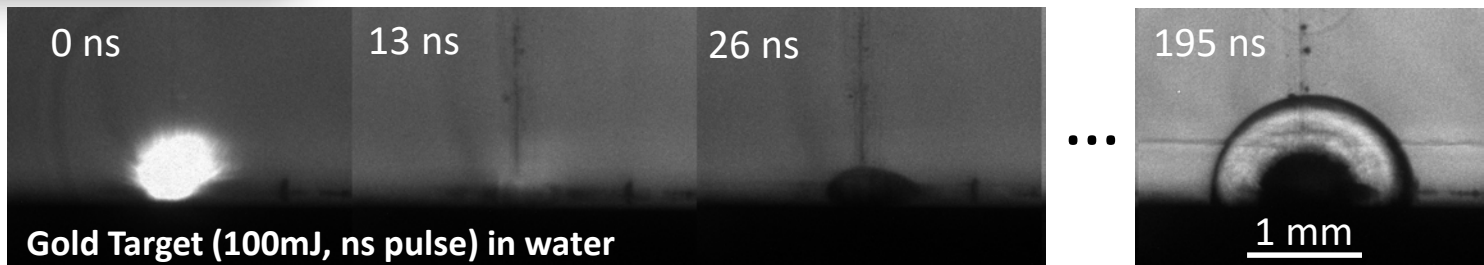


Shadowgraph imaging using a fast camera (210 000 fps)

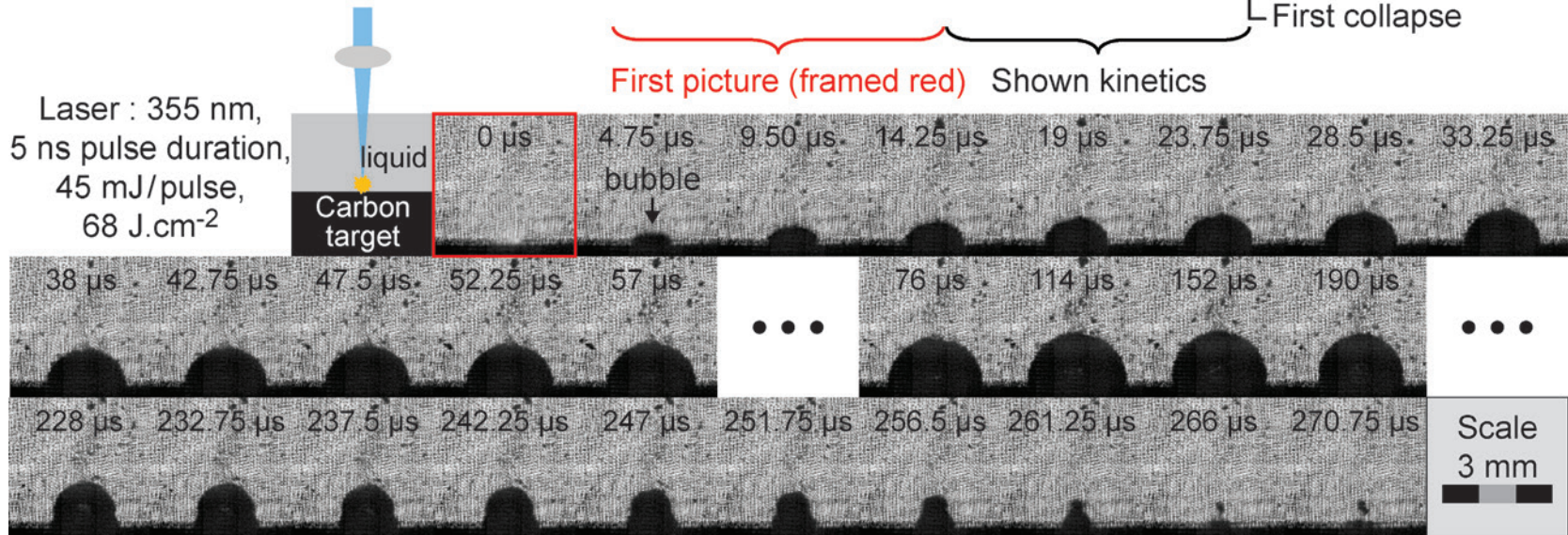
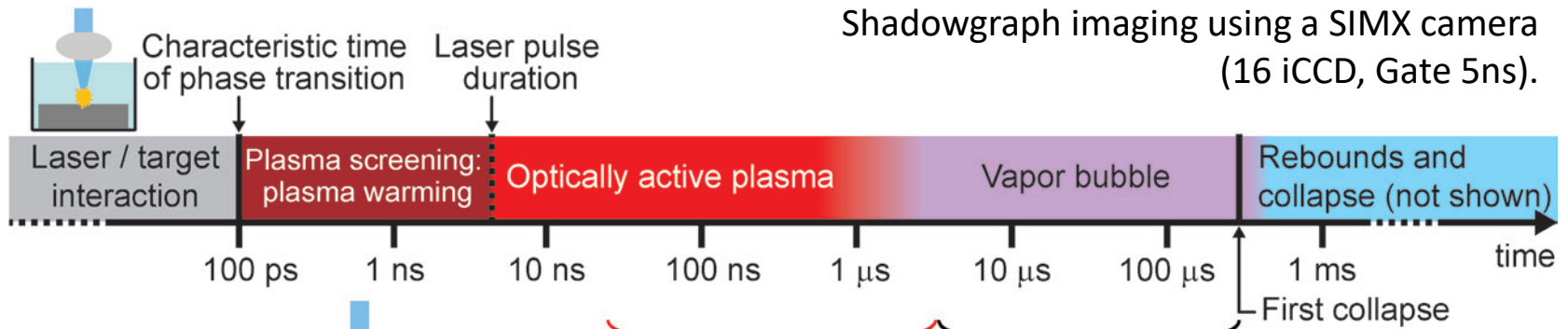


Gold target in water

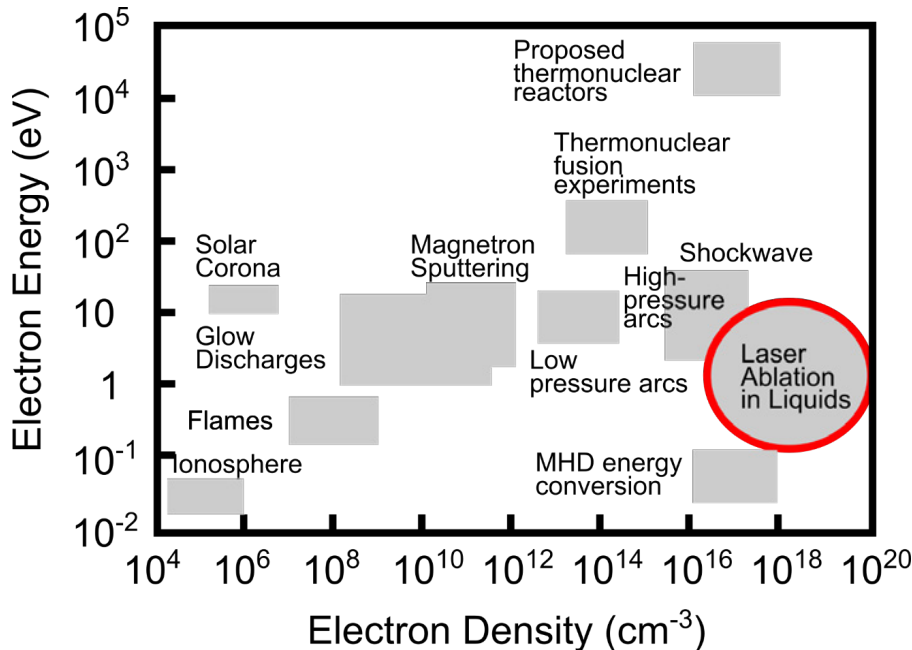
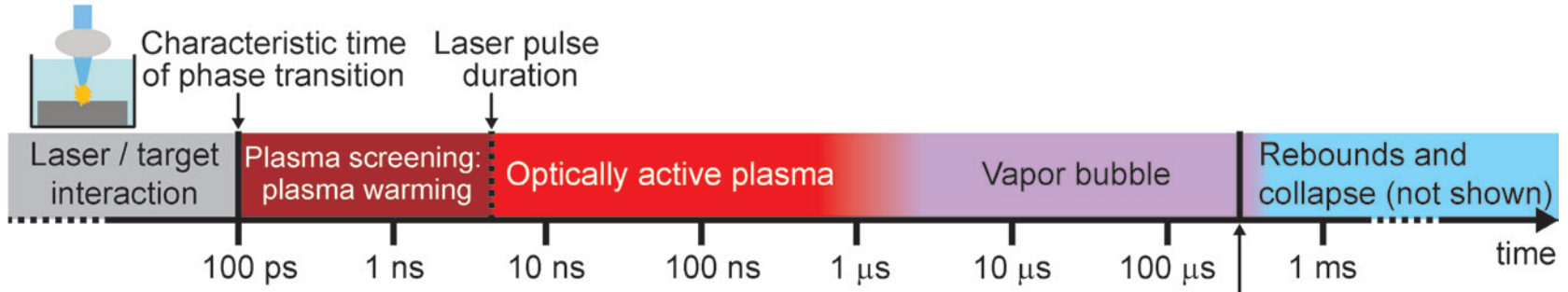




Shadowgraph imaging using a SIMX camera (16 iCCD, Gate 5ns).

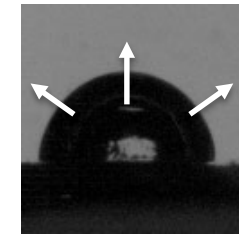


Shadowgraph imaging with fast camera

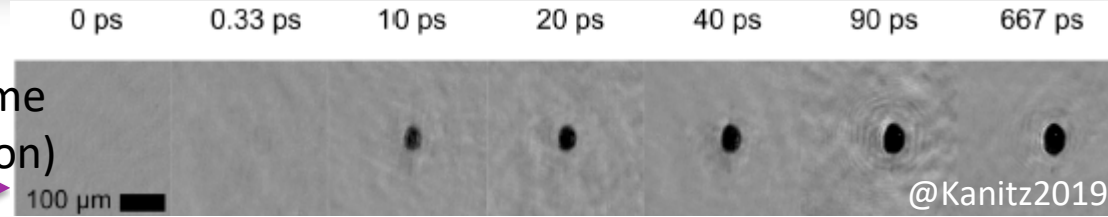


## Original condition:

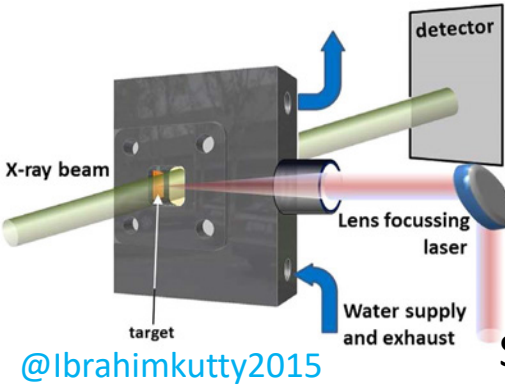
- High pressure / Laser shock peening
- Fast cooling ( a few μs vs. a few tens of μs in air)
- New category of plasma ( $T_e, N_e$ )
- Plasma-liquid interaction ?
- Original Cavitation (high Re, We and Ca)







Pump-probe microscopy<sup>(24-25)</sup> (charac. time e-/phonon, heat diffusion, phase transition)



Rayleigh-Mie scattering<sup>(12,13)</sup> (density, growth kinetics),  
Raman<sup>(19)</sup> (crystal structure)

small angle X-ray scattering<sup>(1,18)</sup> (particles diameter larger than few nm)

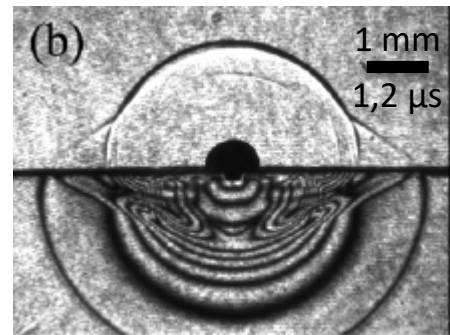
Shadowgraph<sup>(21,22)</sup> and Schlieren imaging<sup>(23)</sup> (shock waves)

acoustic signals<sup>(9-11)</sup> (shock waves release, cavitation lifetime)

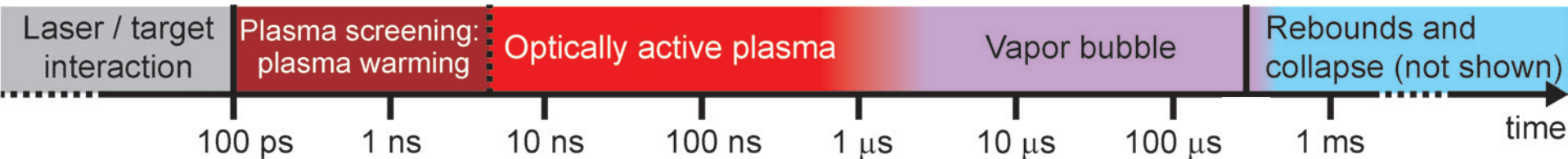
Plasma Imagery<sup>(3-5,17)</sup> and shadowgraph fast imaging<sup>(2, 6-9,20)</sup> (P, V...)

Plasma spectroscopy<sup>(12,14-16)</sup> (species, T, electron density ...)

Light induced fluorescence (species, T)

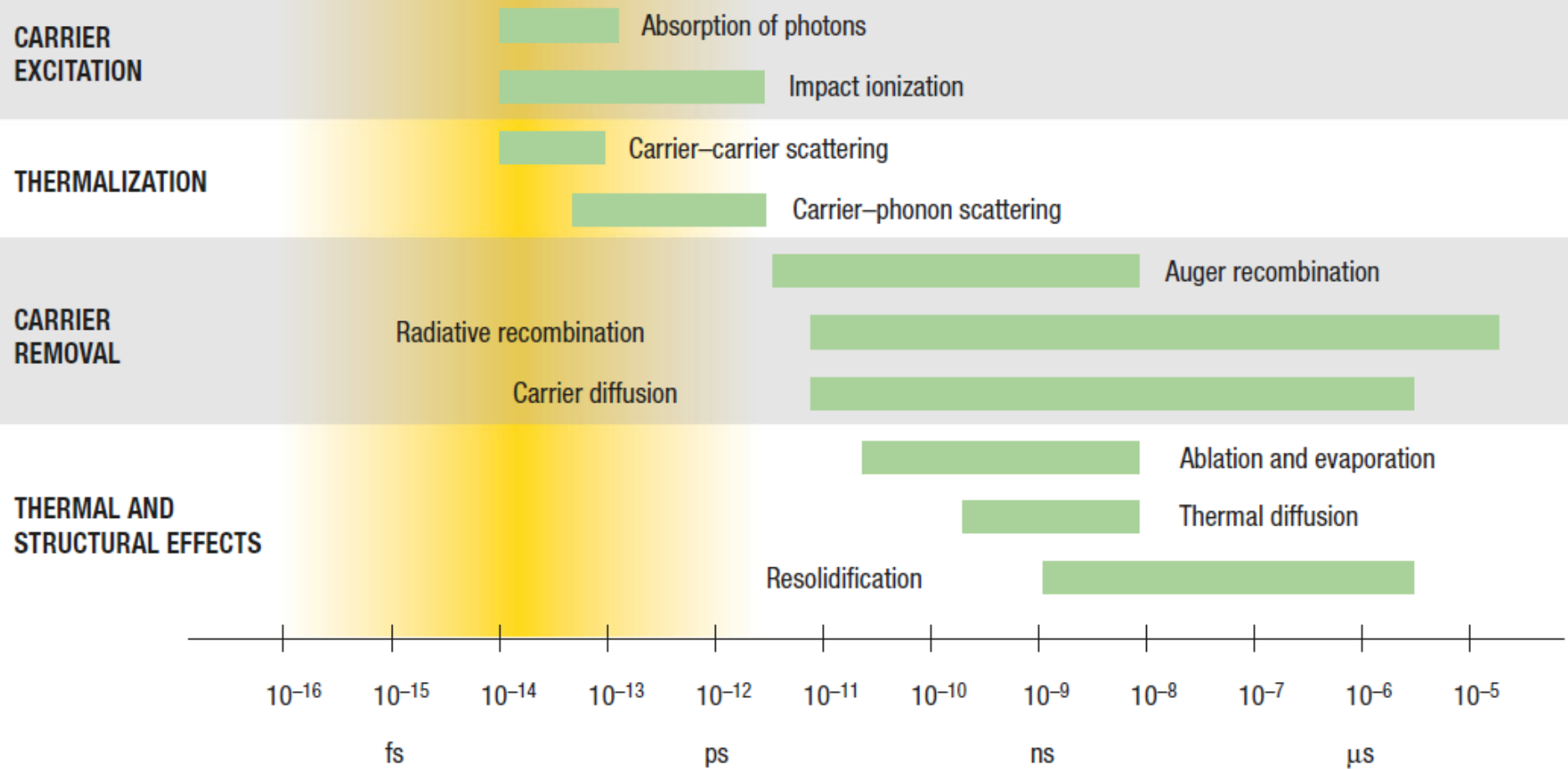


@Nguyen2013



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  - (2) T. Sakka *et al.*, Spectrochim. Acta, Part B **64**, 981 (2009).
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  - (10) H. Jin *et al.*, Phys. Chem. Chem. Phys. **12**, 5199–5202 (2010).
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  - (15) J. Lam *et al.*, Phys.Chem.Chem.Phys. **16**, 963 (2014)
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  - (22) Z. Zhang *et al.*, AIP Advances **9**, 125048 (2019)
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- [25bis] S. Rapp, M. Kaiser, M. Schmidt, H.P. Huber, Ultrafast pump-probe ellipsometry setup for the measurement of transient optical properties during laser ablation, Opt.Express **24** (16) (2016) 17572–17592, <https://doi.org/10.1364/OE.24.017572>.

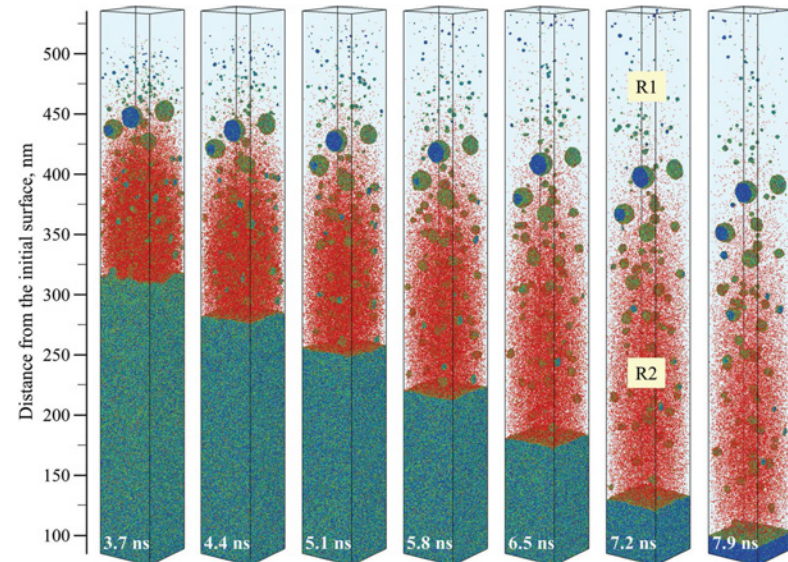
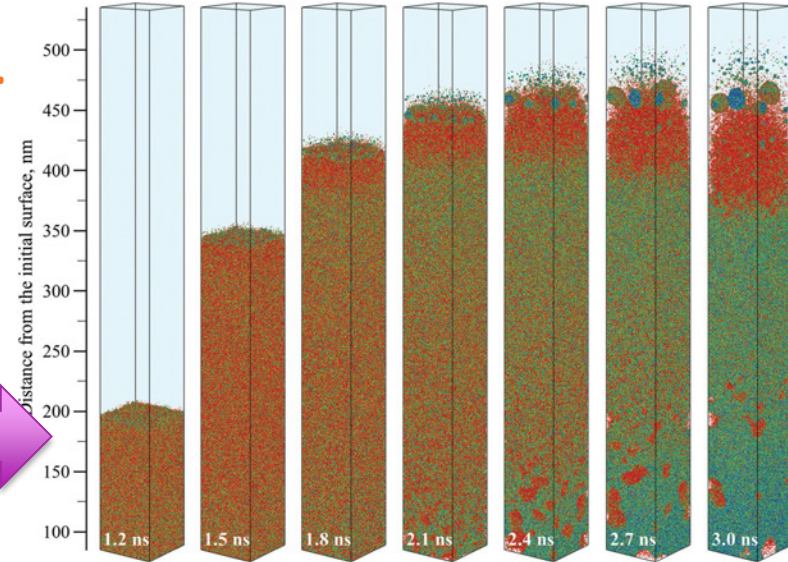
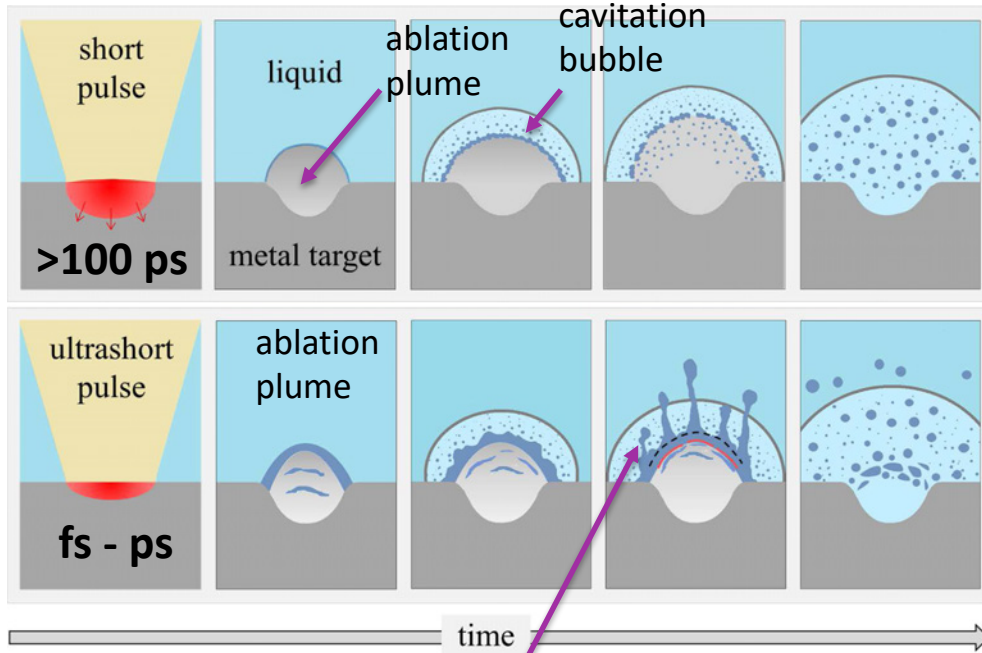
**Non-exhaustive list !  
Ask me !**





Ag target, 400ps, 600 mJ/cm<sup>2</sup>, box size 50 nm x 50 nm  
Molten Ag (blue) / Vapor-phase Ag atoms (red)

- ✓ Early appearance of the nanoparticles (first few ns).
- ✓ Bimodal size distribution: Two mechanisms of nanoparticle generation in laser ablation in liquids.



Jetting of the molten metal (Richtmyer–Meshkov instability) from the layer roughened by Rayleigh–Taylor instability

## Basic question: Why do we observe multimodal size distribution even in flow chamber?

No post-processes

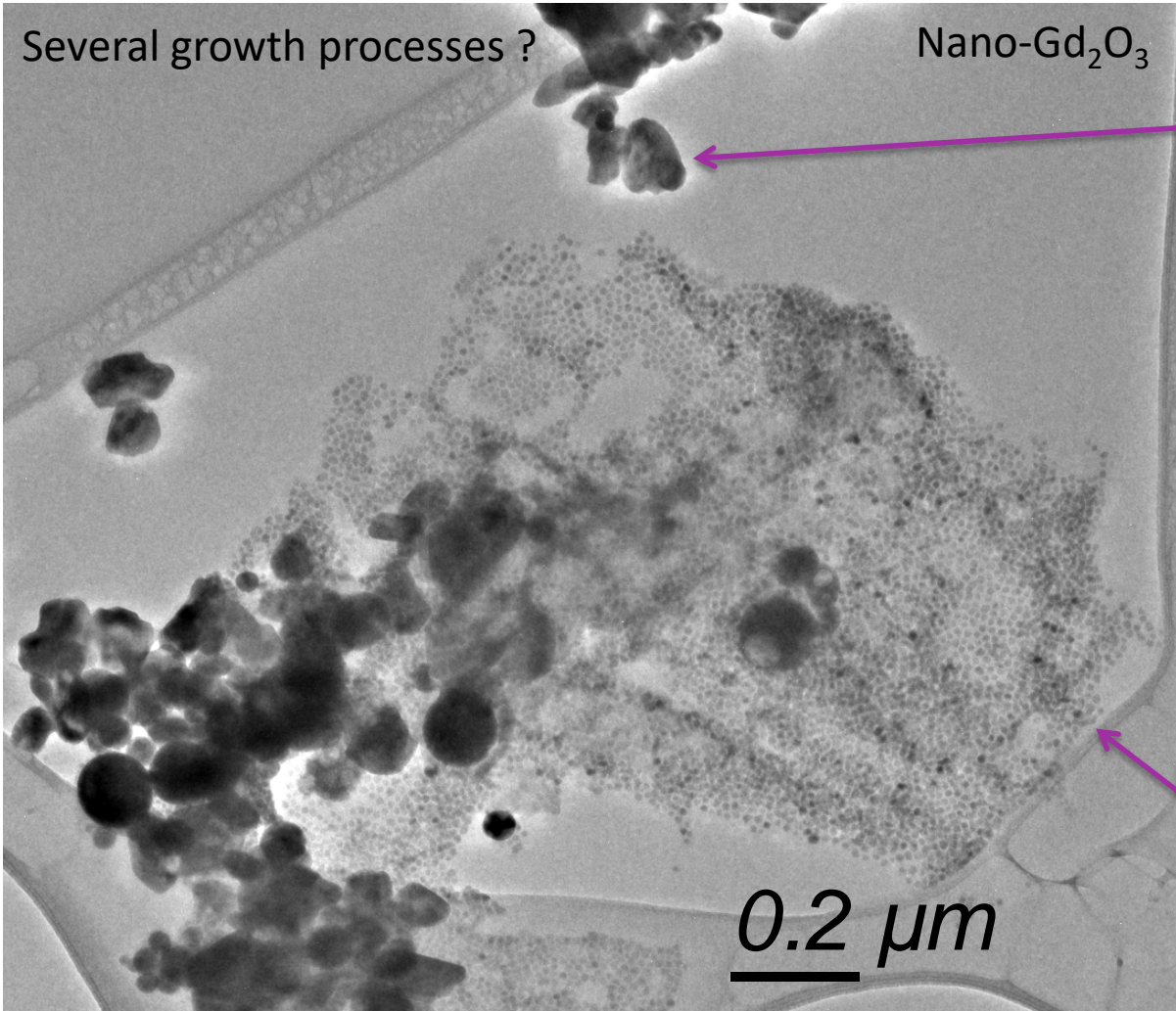
Several growth processes ?

Nano-Gd<sub>2</sub>O<sub>3</sub>

“Big” particles: Phase transition of the target (lift-off) ?

“Small” particles: Nucleation and growth from the plasma ?

0.2 μm

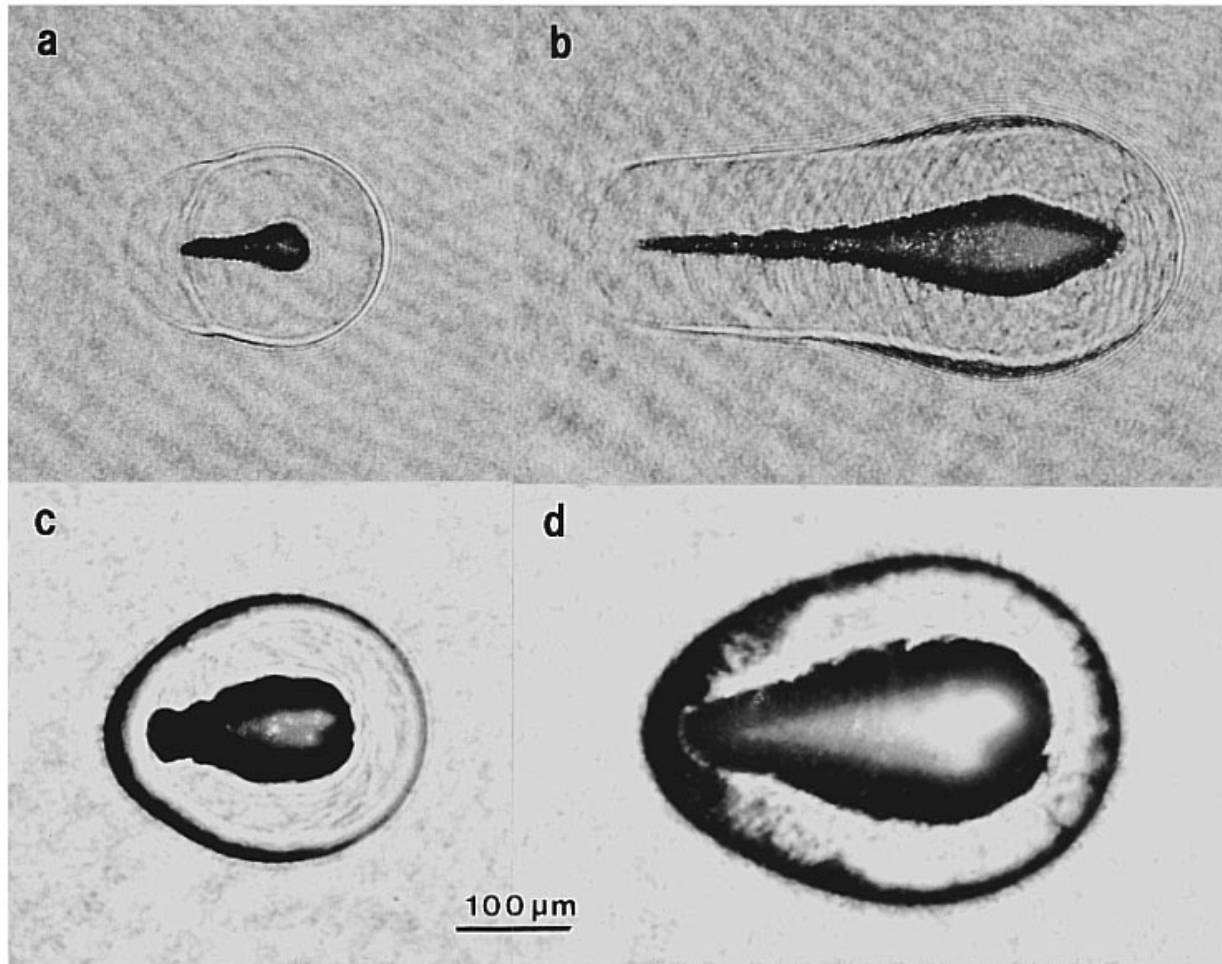


## Shock waves

- **Shock waves kinetics and pressure measurement**
- **Fabbro & Berthe's model**
- **Surface waves and elastic modulus measurement**



## Bibliography: Alfred Vogel (Univ. Lübeck) , Werner Lauterborn (Univ. Göttingen)



Plasma, shock wave, and cavitation bubble produced by Nd:YAG laser pulses of different duration and energy:

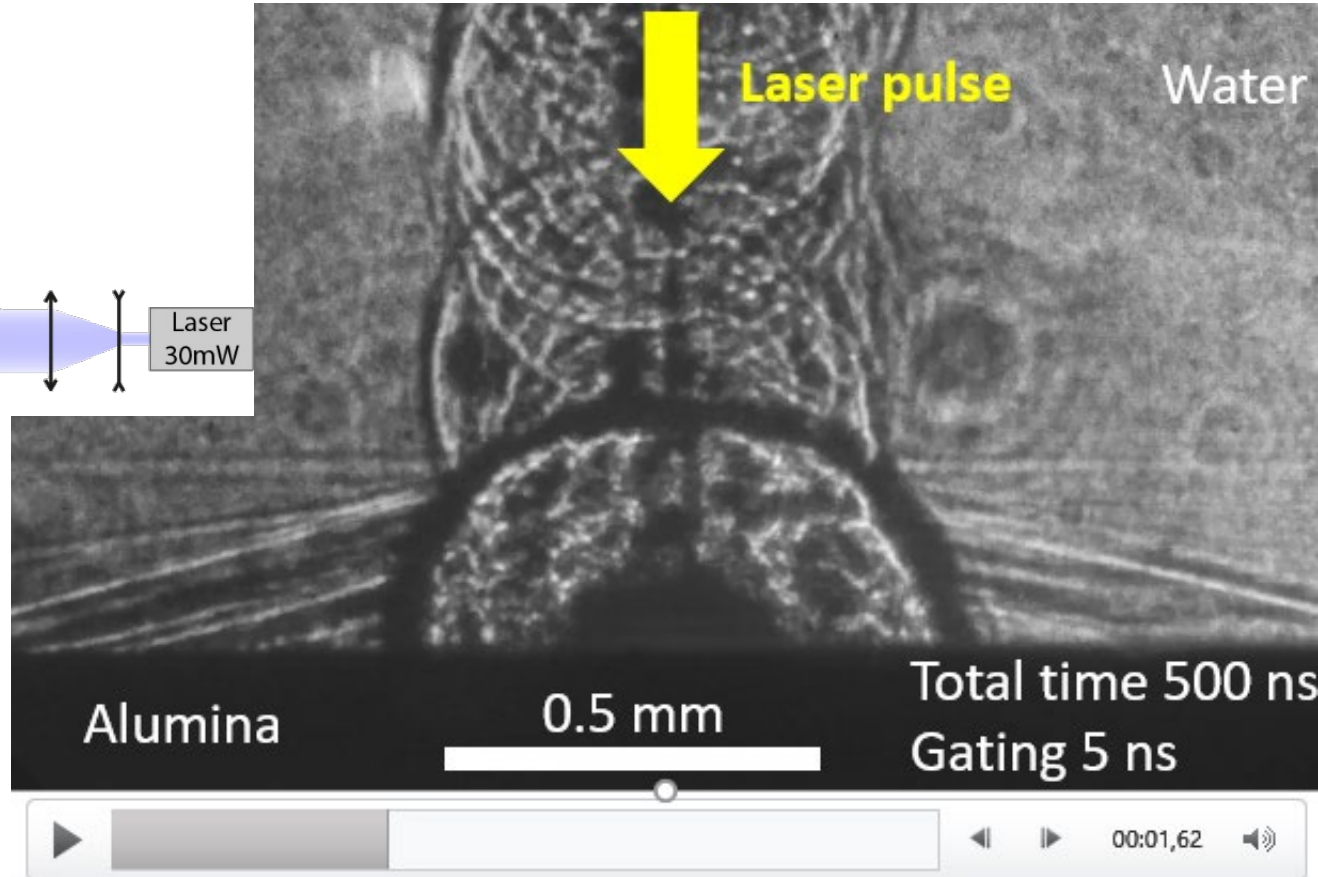
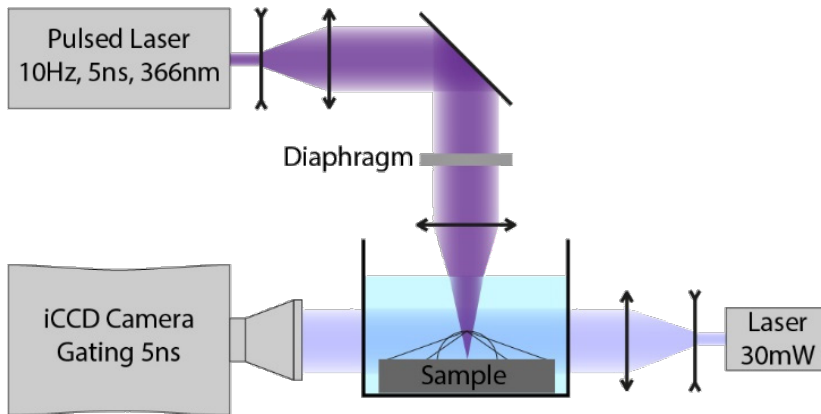
(a) 30 ps, 50  $\mu$ J;

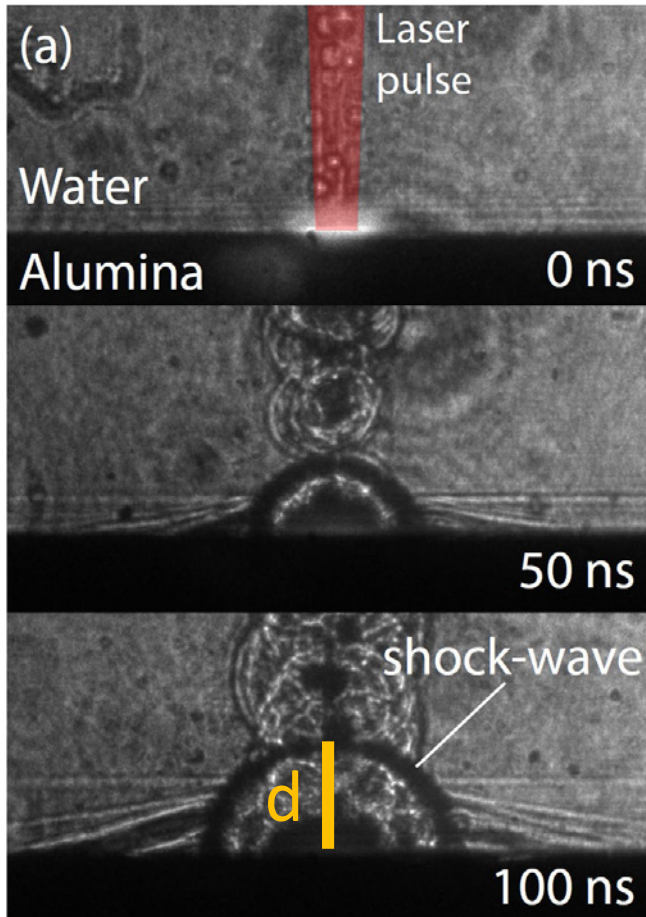
(b) 30 ps, 1 mJ;

(c) 6 ns, 1 mJ;

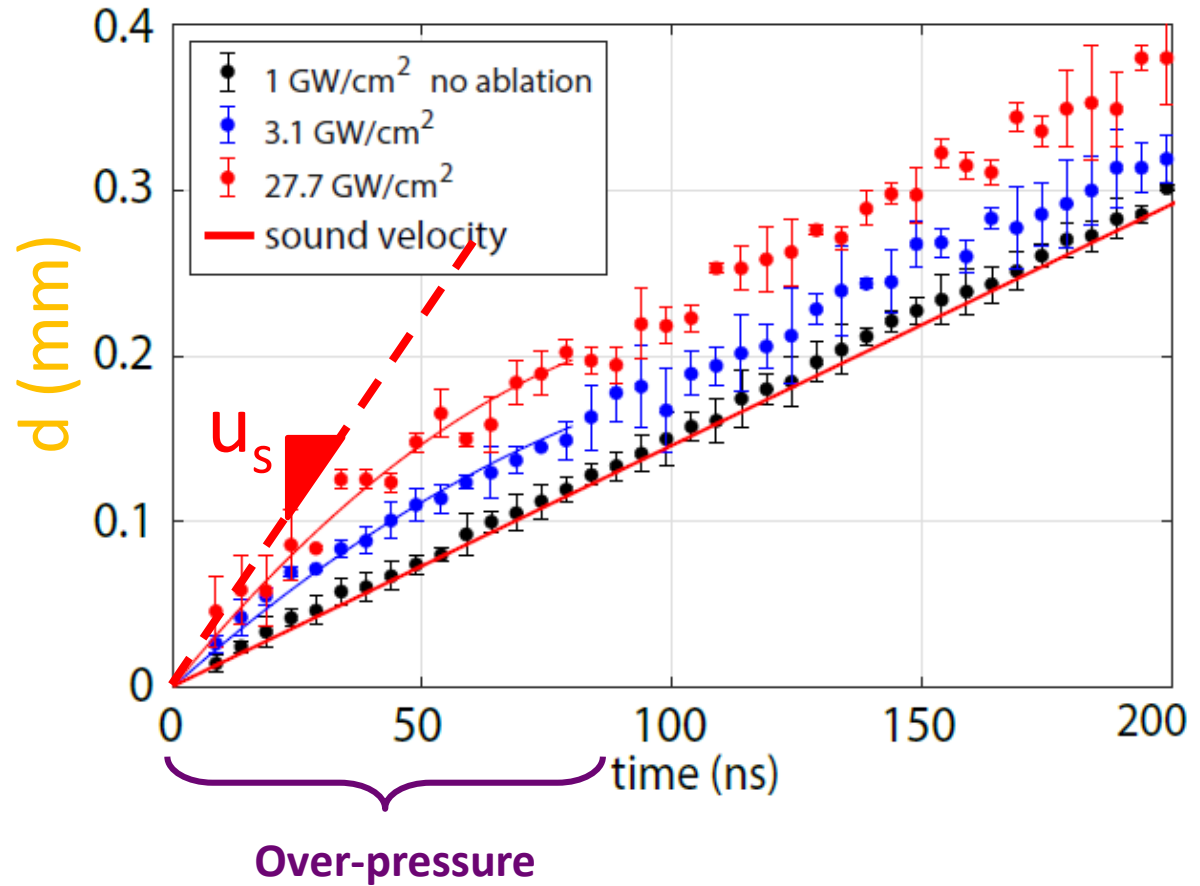
(d) 6 ns, 10 mJ.

All pictures were taken **44 ns** after the optical breakdown.





## Shock front kinematics



Conservation of momentum  
at a shock front:

$$p_s - p_\infty = u_s u_p \rho_0$$

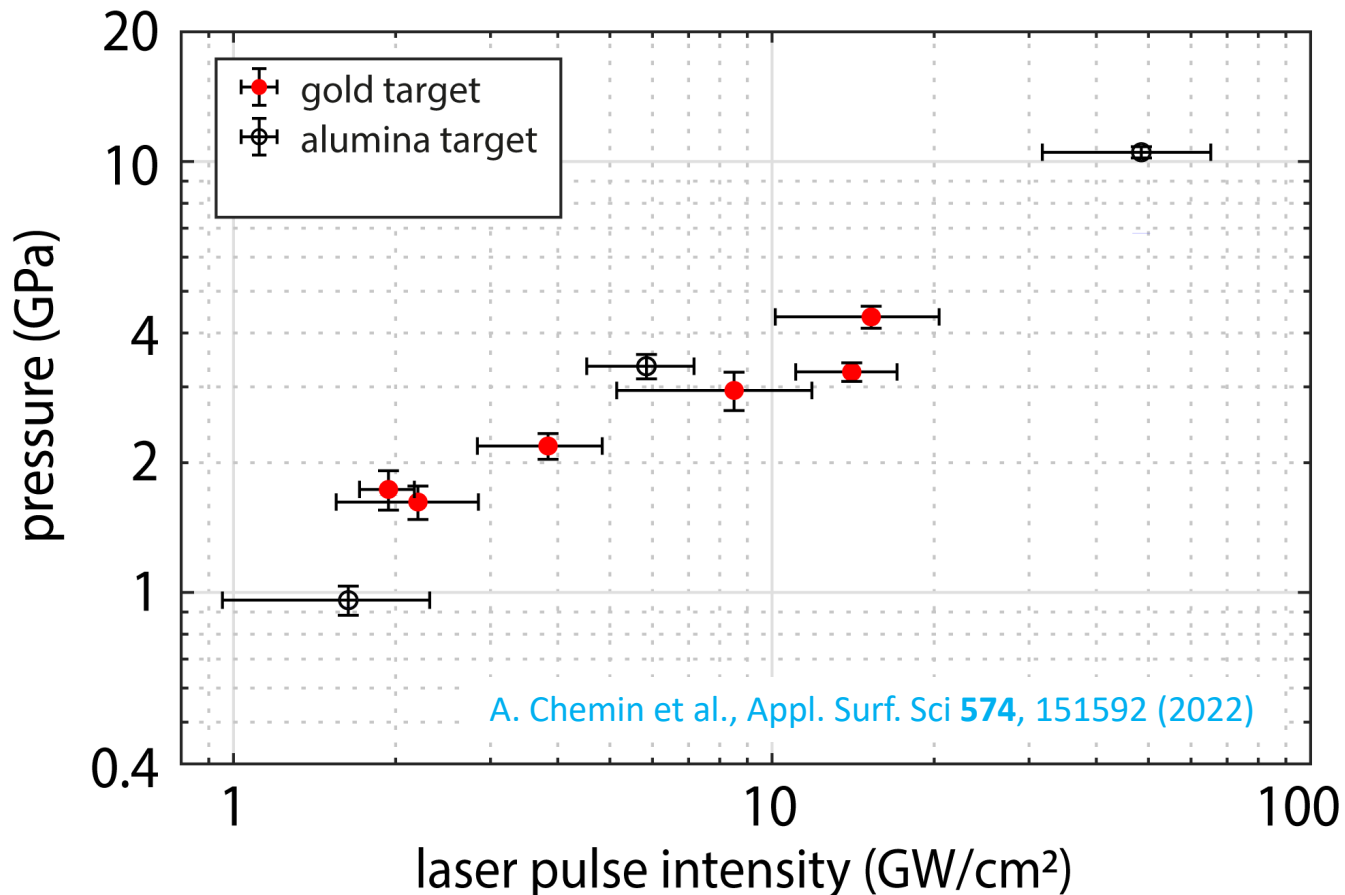
$u_p$  : particles velocity

Hugoniot curve from Rice and Walsh:

$$u_p = c_1 \left( 10^{\frac{u_s - c_0}{c_2}} - 1 \right)$$

$$c_1 = 5190 \text{ m/s} ; c_2 = 25\,306 \text{ m/s}$$

Valid up to 25 GPa



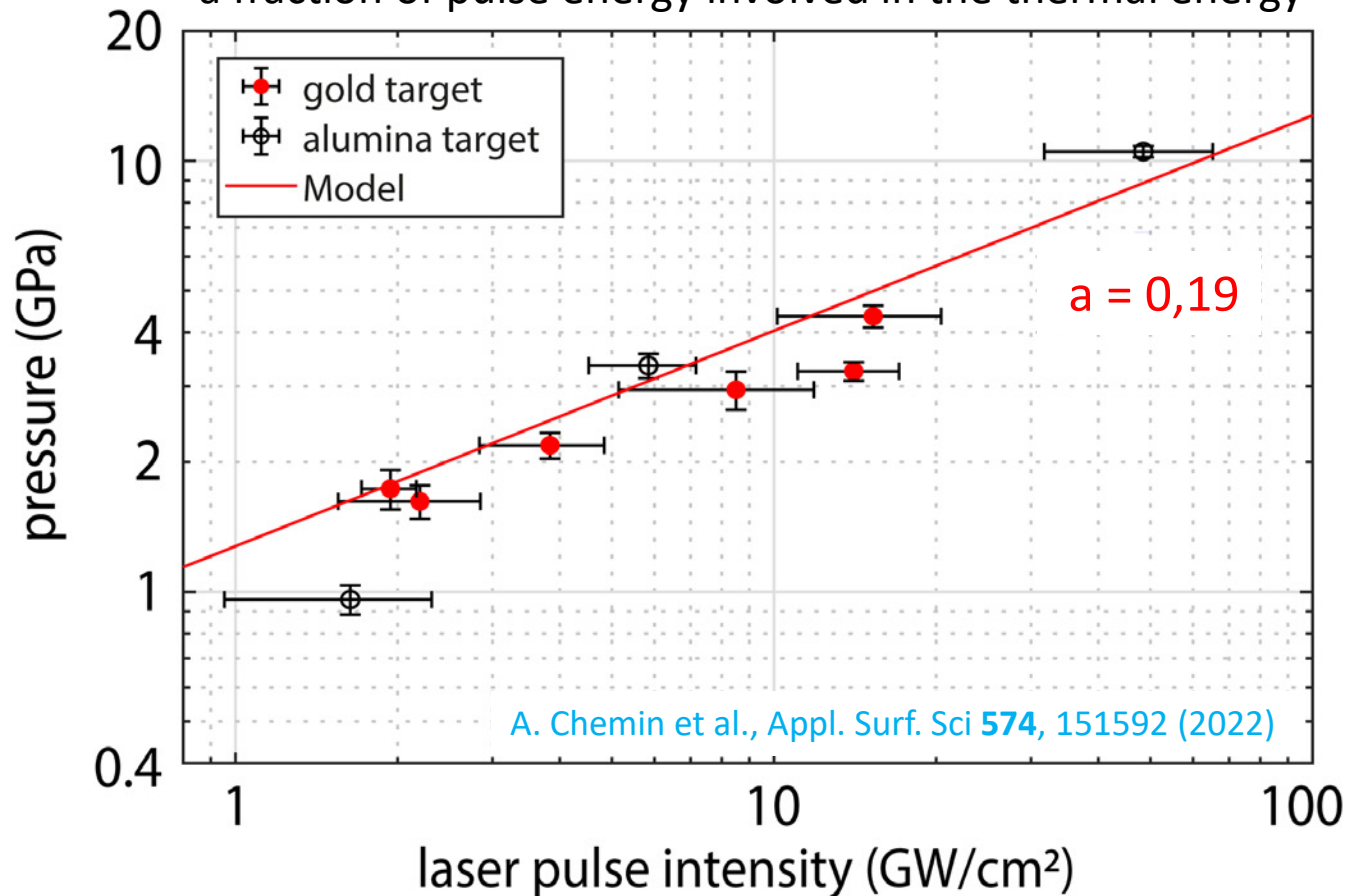


Relates the initial pressure to the pulse energy :  $p_s(\text{MPa}) = 10 \sqrt{\frac{a}{2a+3}} ZI$   
 R. Fabbro et al. J. Appl. Phys. **68**, 775 (1990)

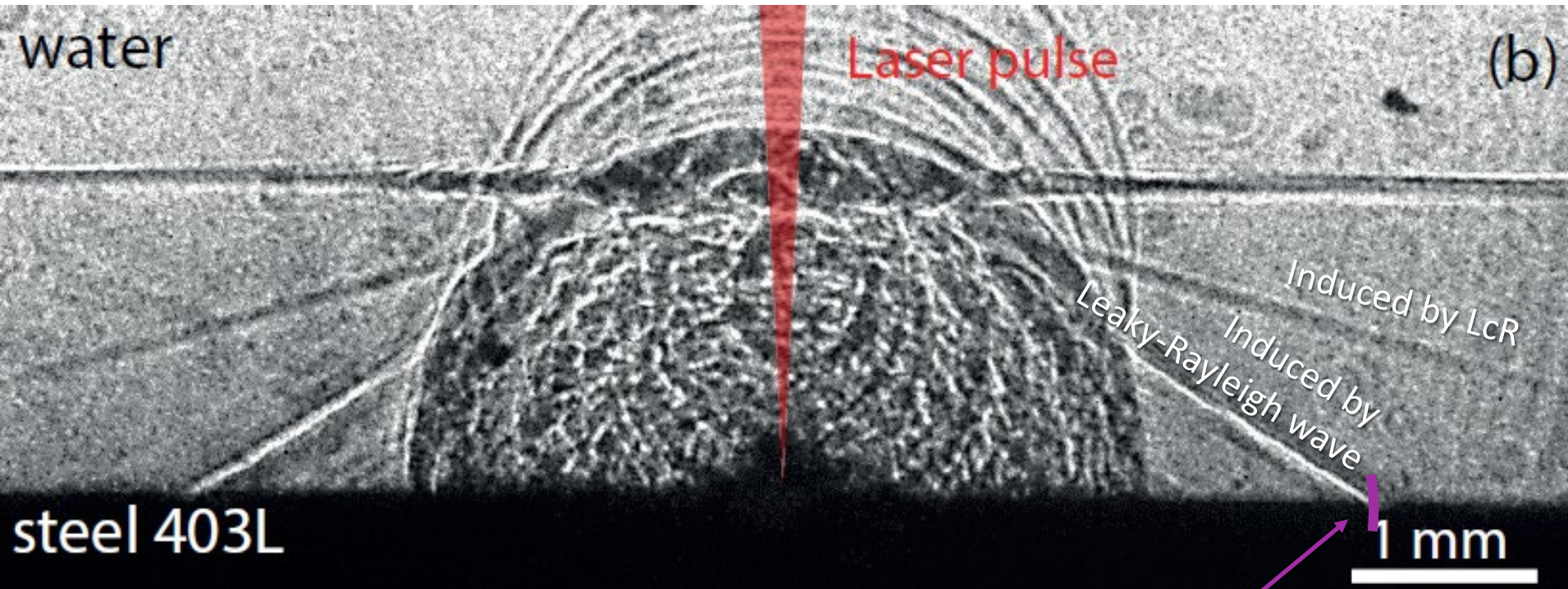
$Z$  the reduced acoustic impedance

$I$  the laser intensity [ $\text{W}/\text{cm}^2$ ]

$a$  a fraction of pulse energy involved in the thermal energy



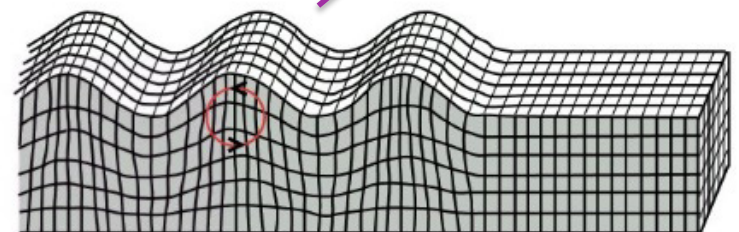
# Origin the observed shock waves ?



“Mach” cone induced by:

- **Critically refracted longitudinal (LCR) wave**
- **Surface waves** at the interface between the liquid and the target: **the leaky-Rayleigh wave**

Rayleigh Wave



# Measurement of elastic modulus (E, ν)

Leaky  
Rayleigh  
wave

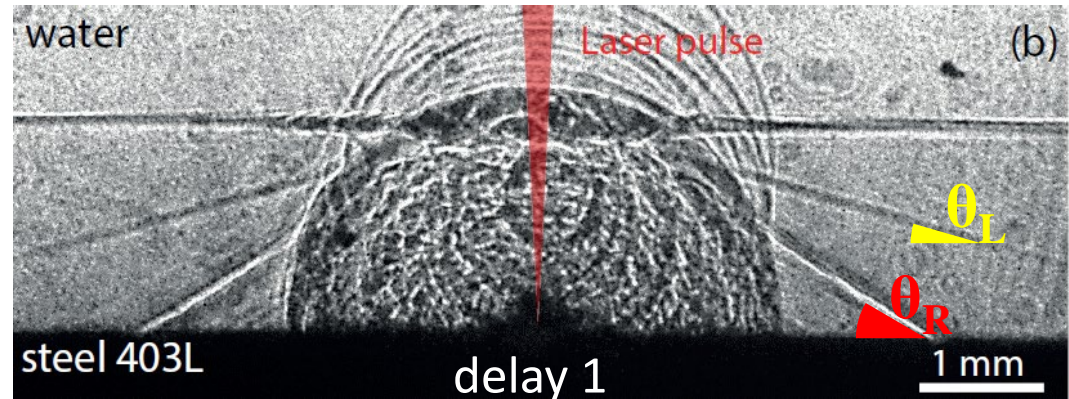
Measurement

$$\sin(\theta_R) = \frac{c_0}{c_R}$$

$$\sin(\theta_L) = \frac{c_0}{c_L}$$

LcR

$c_0$  sound velocity



Rayleigh's approx.

In vacuum:

$$c_R = c_T \sqrt{\frac{28\nu + 22}{21\nu + 29}}$$

Wave velocities vs elastic modulus

For isotropic materials:

$$c_T = \sqrt{\frac{1}{2(1+\nu)} \frac{E}{\rho}} \quad c_L = \sqrt{\frac{1-\nu}{(1+\nu)(1-2\nu)} \frac{E}{\rho}}$$

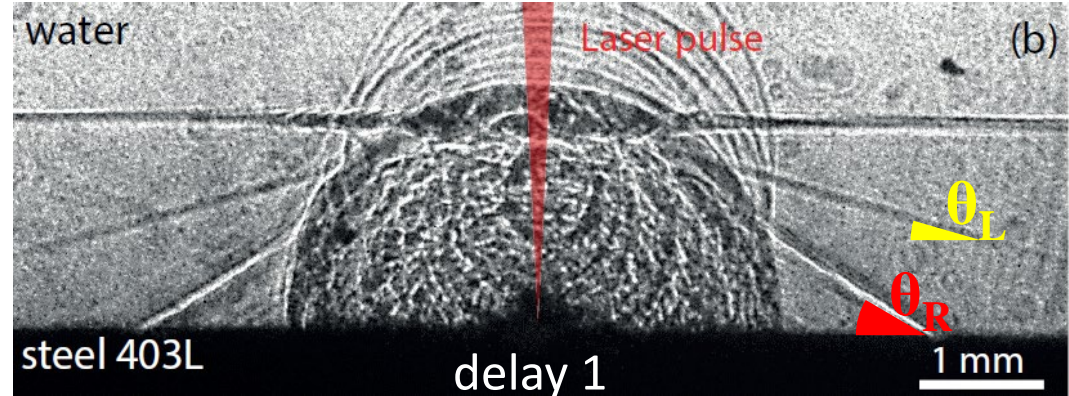


# Measurement of elastic modulus (E, ν)

## Measurement

$$\sin(\theta_R) = \frac{c_0}{c_R}$$

$$\sin(\theta_L) = \frac{c_0}{c_L}$$



## Determination of ν

$$\left( \frac{\sin(\theta_L)}{\sin(\theta_R)} \right)^2 = \frac{1 - 2\nu}{2(1 - \nu)} \times \frac{28\nu + 22}{21\nu + 29}$$

## Determination of E/ρ

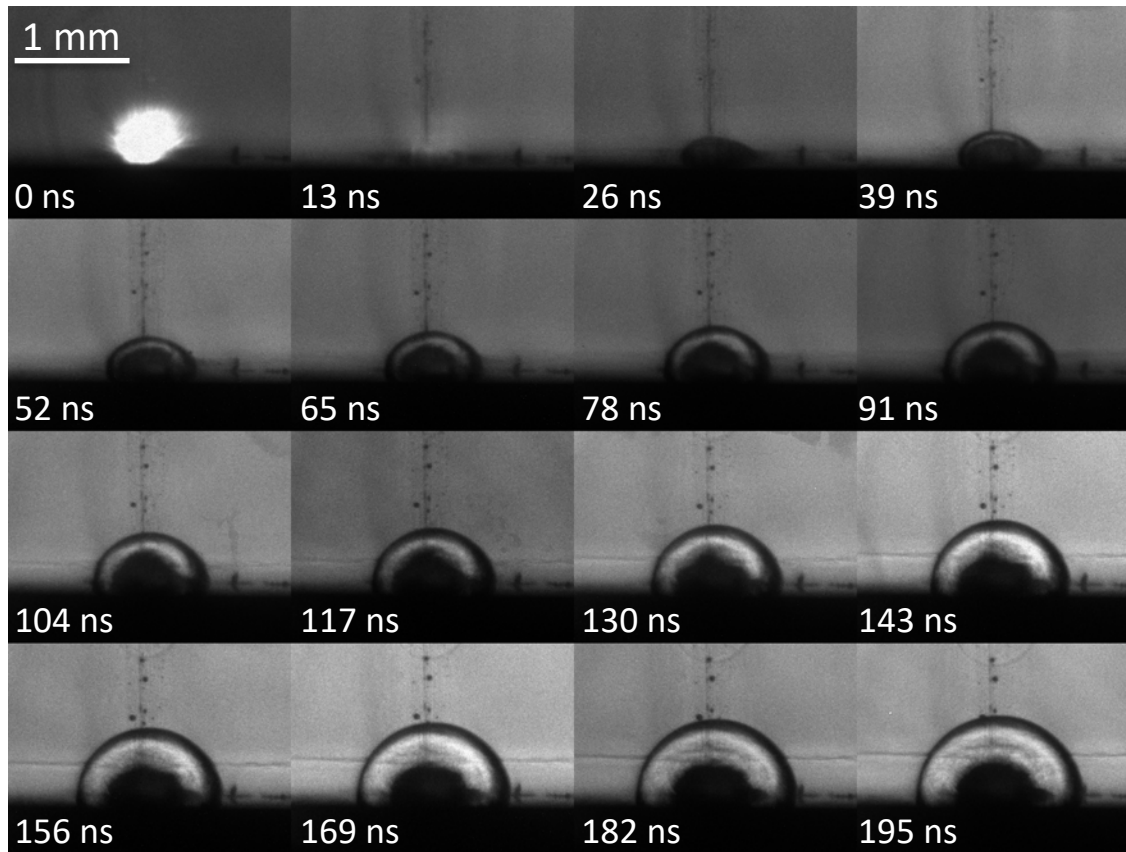
$$\frac{E}{\rho} = \frac{(1 + \nu)(1 - 2\nu)}{1 - \nu} \left( \frac{c_0}{\sin(\theta_L)} \right)^2$$

Depends only on the angles!

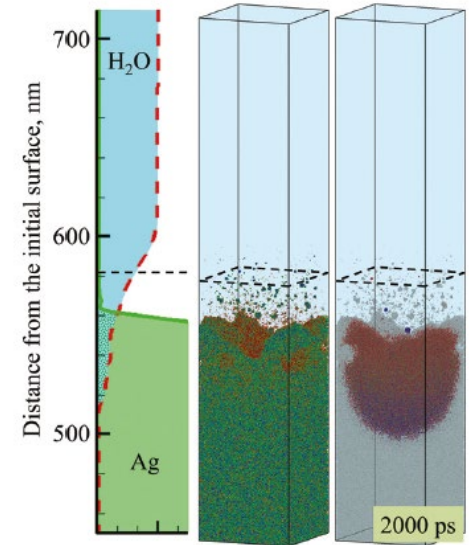


Plasma/liquid interaction and bubble formation

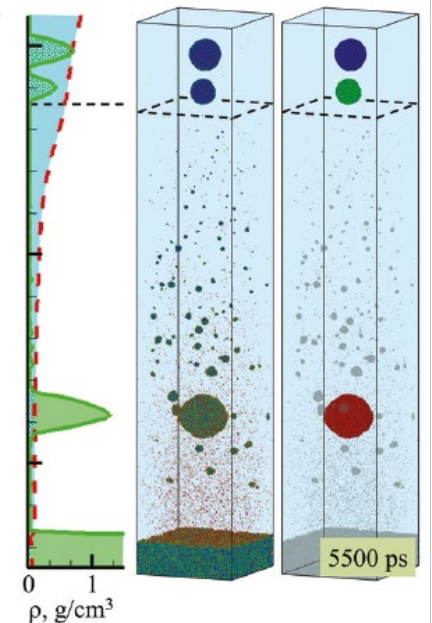
*Shock-bag @ ESRF (July 2023)*



Shadowgraph imaging using a SIMX camera (16 iCCD, Gate 5ns).



Consistency with molecular dynamics ?

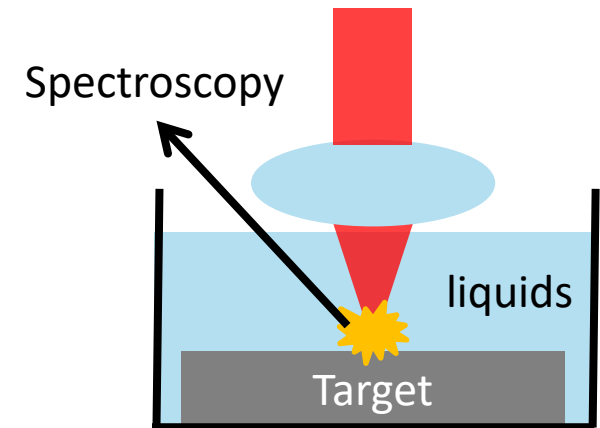


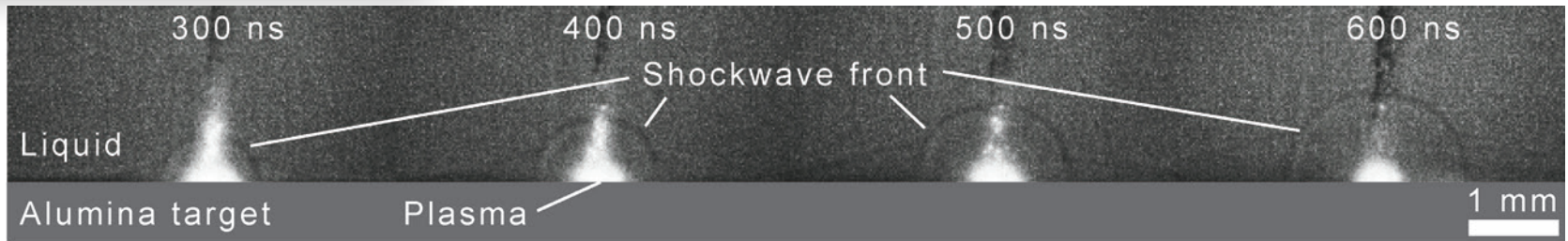
# Plasma spectroscopy

- **Overview**
- **Temperatures**
- **LIF measurement**

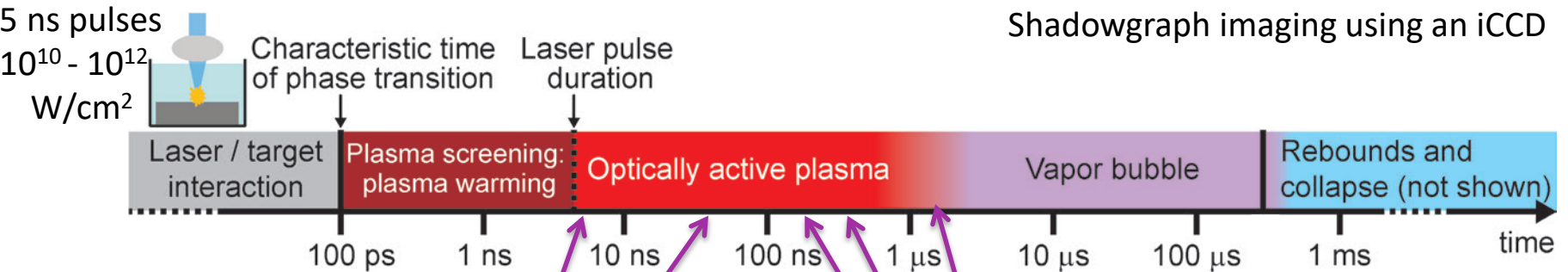
## Plasma spectroscopy : measurement of thermodynamic parameters

- **Plasma species and time evolution of the chemical composition**  
atomic / ionic / diatomic molecules
- **Plasma temperatures**  
diatomic molecules :  $T_{\text{rotational}}$ ,  $T_{\text{vibrational}}$   
Electronic temperature of atoms, ions molecules :  $T_{\text{elec}}$   
(electrons (kinetics) :  $T_e$ )
- **Electron density ( $n_e$ ):**  
Electronic field => Stark effects (broadening and shift)

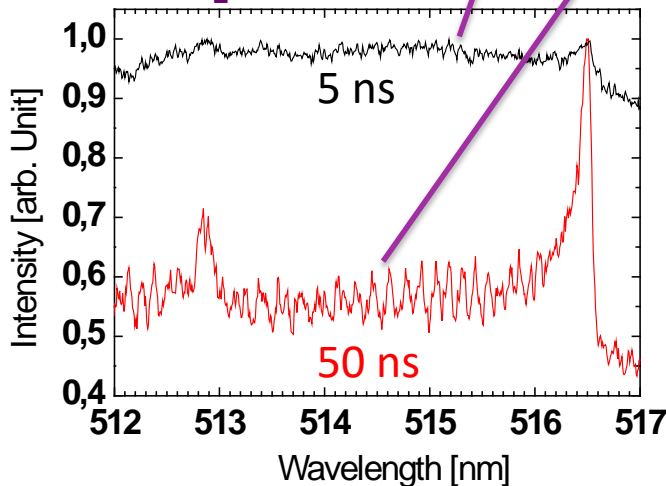




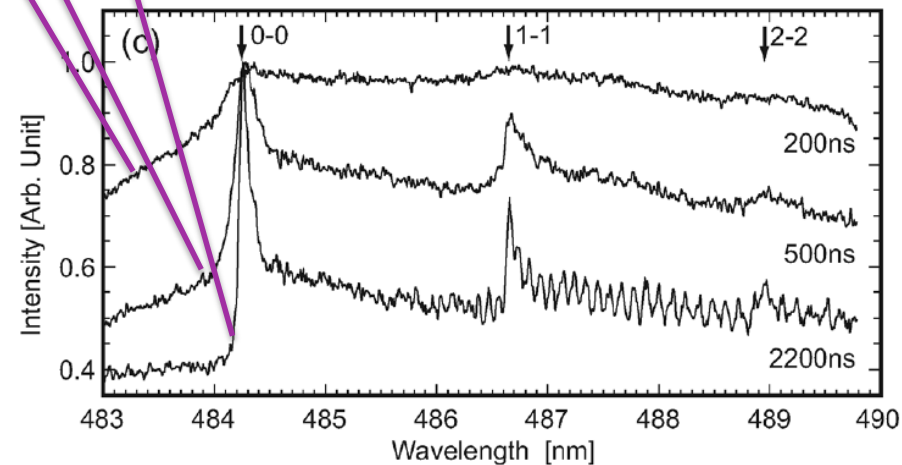
Shadowgraph imaging using an iCCD



Carbon target -> C<sub>2</sub> swan band



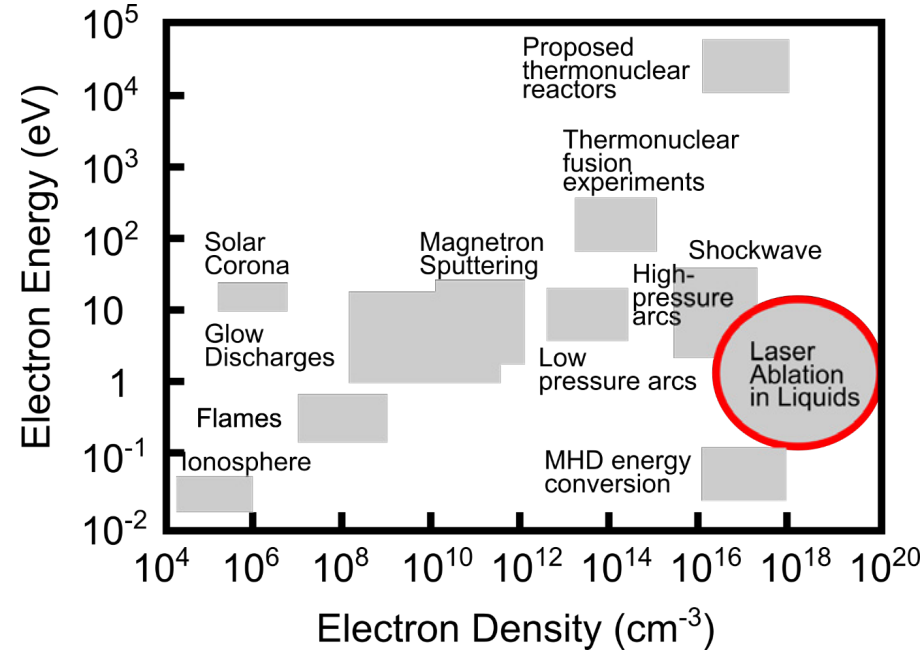
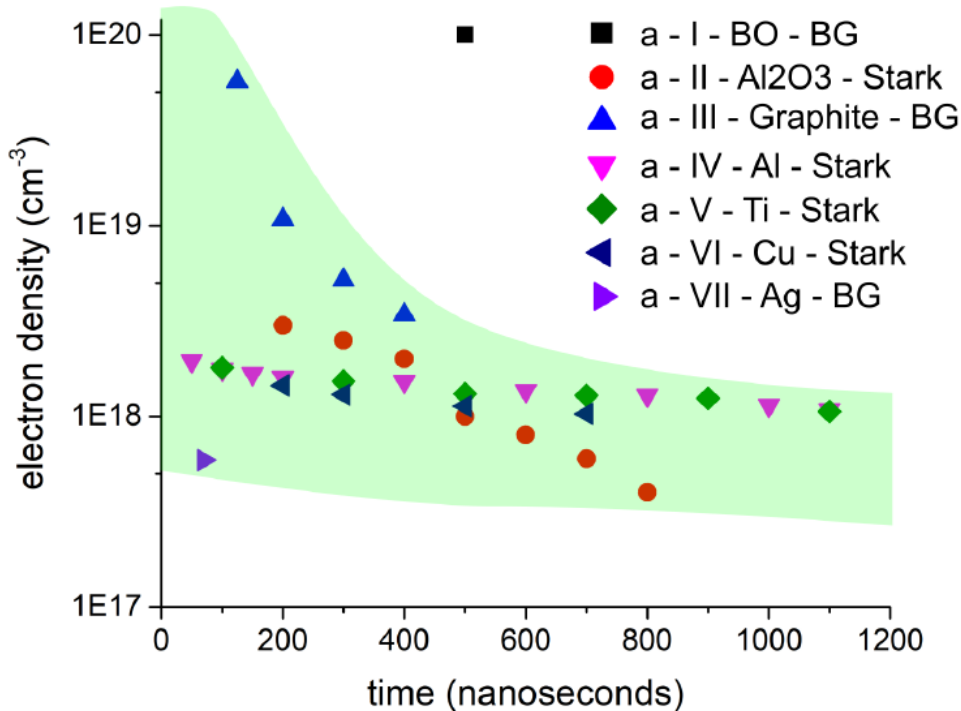
Al<sub>2</sub>O<sub>3</sub> target -> AlO molecules



Molecules appear early (with respect to what is observed in gas or vacuum) -> problem for LIBS



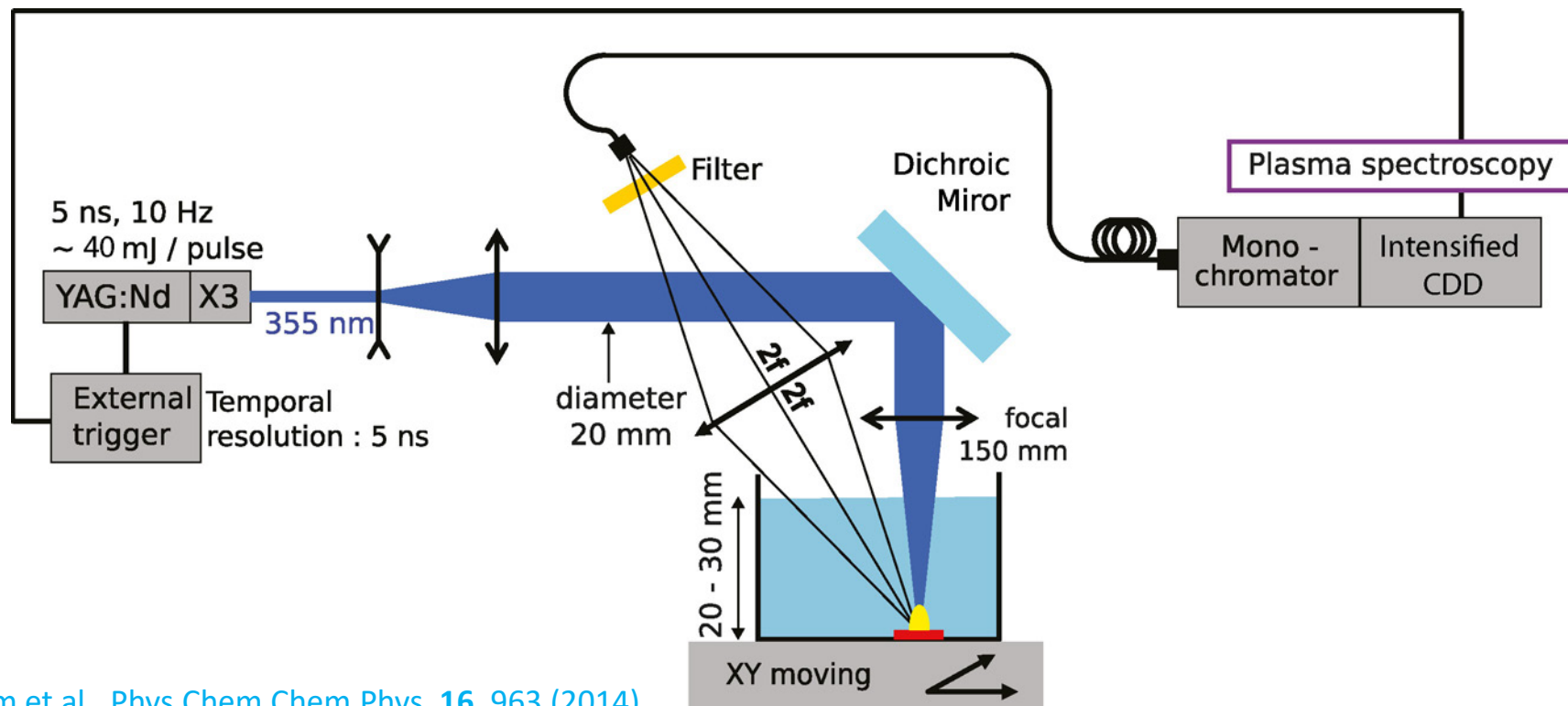
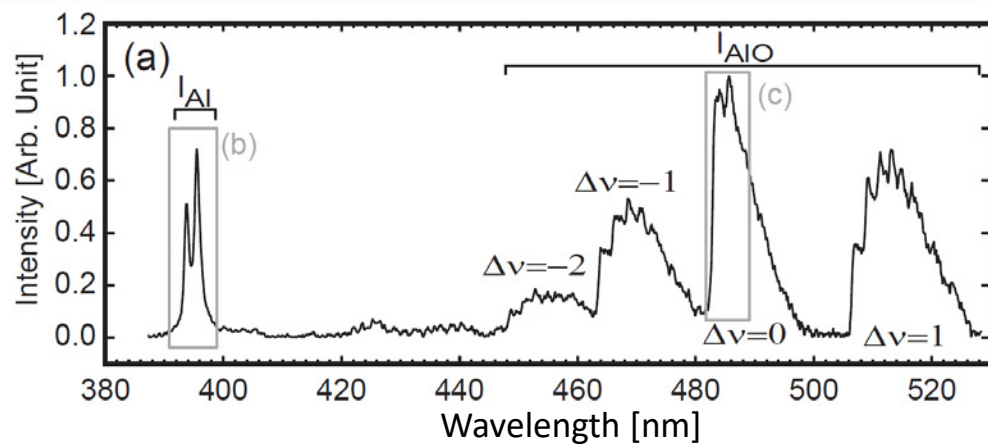
BG : Background emission  
Stark : Stark shift/broadening



Here... good news for what concerns  
the local thermodynamic equilibrium  
for the electronic states

$$N_e \geq 6.5 \times 10^{16} \times \frac{g_{max}}{g_{min}} \left( \frac{\Delta E}{E_1^H} \right)^3 \left( \frac{kT_{elec}}{E_1^H} \right)^{0.5} \Phi_1 \left( \frac{\Delta E}{kT_{elec}} \right)$$

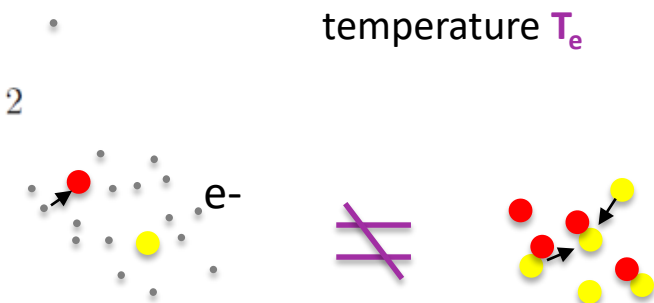
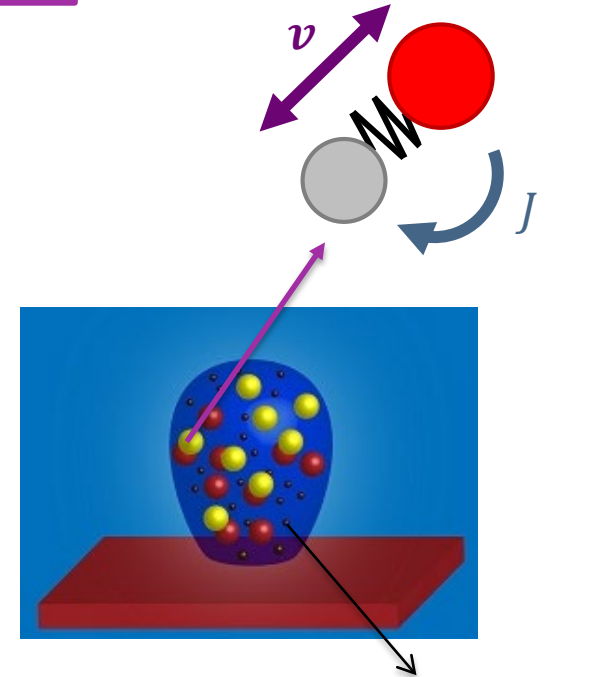
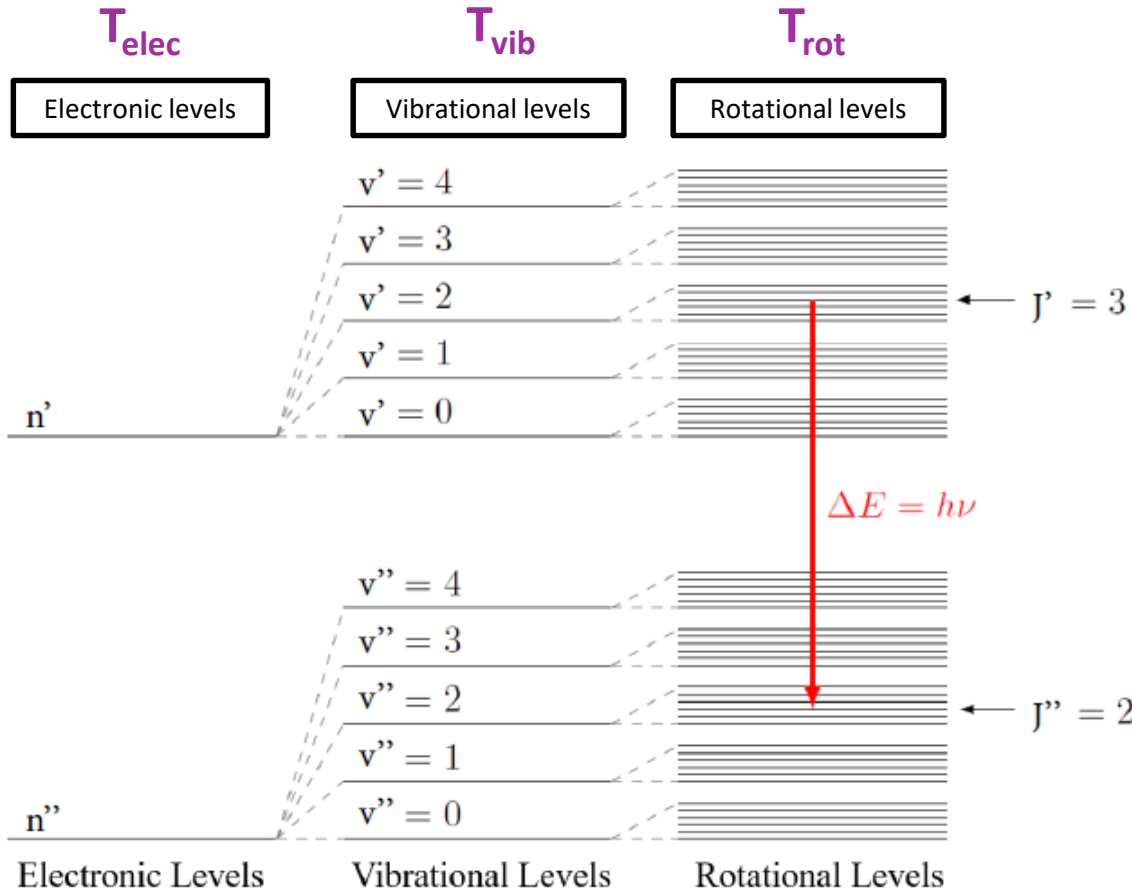
Exemple on  $\text{Al}_2\text{O}_3$  target



## Temperatures:

- Atoms :  $T_{elec}$
- Diatomic molecules :  $T_{elec}$  ,  $T_{vib}$  ,  $T_{rot}$

canonical ensemble



$E = T_n + G_n(v) + F_v(J)$  ... but  $F_v(J)$  Depend on the Hund's case ( $\vec{S}, \vec{L}, \vec{N}$  and their projection)

Istvan Kovacs (1969)

$$G_n(v) = w_e \left( v + \frac{1}{2} \right) - w_e x_e \left( v + \frac{1}{2} \right)^2 + w_e y_e \left( v + \frac{1}{2} \right)^3 + \dots \quad (cm^{-1}).$$

$$F_v(J) = B_v \cdot J(J+1) - D_v \cdot \left( J(J+1) \right)^2 + \dots + H(J, K, S, \Lambda, \Sigma \dots) \quad (cm^{-1})$$

} Tabulated

$$I_{n'',v'',J''}^{n',v',J'} = hc \cdot \bar{\nu}_{n'',v'',J''}^{n',v',J'} \cdot A_{n'',v'',J''}^{n',v',J'} \cdot N_{n',v',J'} \quad (W \cdot m^{-3}). \quad \text{Intensity}$$

band strength

Probability of spontaneous transition ( $s^{-1}$ )  $A_{n'',v'',J''}^{n',v',J'} = A_{n'',v''}^{n',v'} \cdot A_{J''}^{J'}$

Einstein Coefficient  $A_{n'',v''}^{n',v'} = \frac{1}{4\pi\epsilon_0} \frac{64\pi^4}{3h(2 - \delta_{0,\Lambda'}) (2S' + 1)} \cdot (100 \cdot \bar{\nu}_{n'',v'',J''}^{n',v',J'})^3 \cdot S_{n'',v''}^{n',v'} \cdot (a_0 e)^2$

$A_{J''}^{J'} = \frac{S_{J''}^{J'}}{2J' + 1}$  ← Höln-London's coefficient

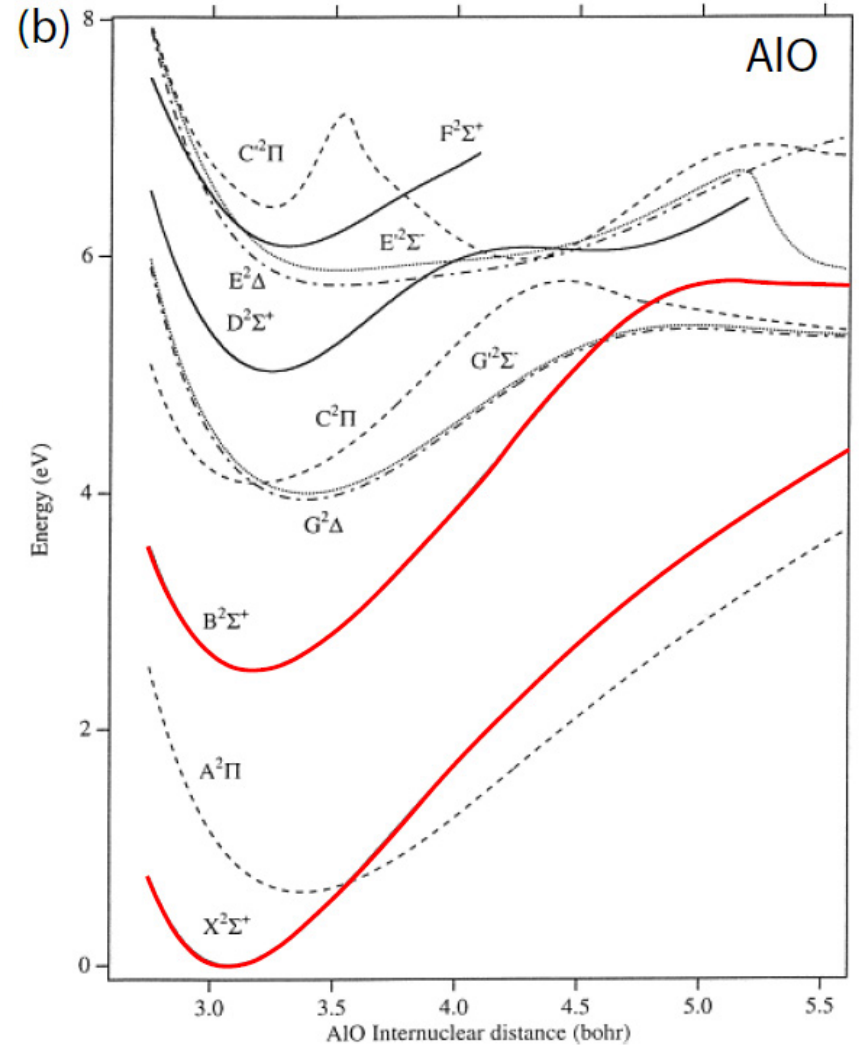
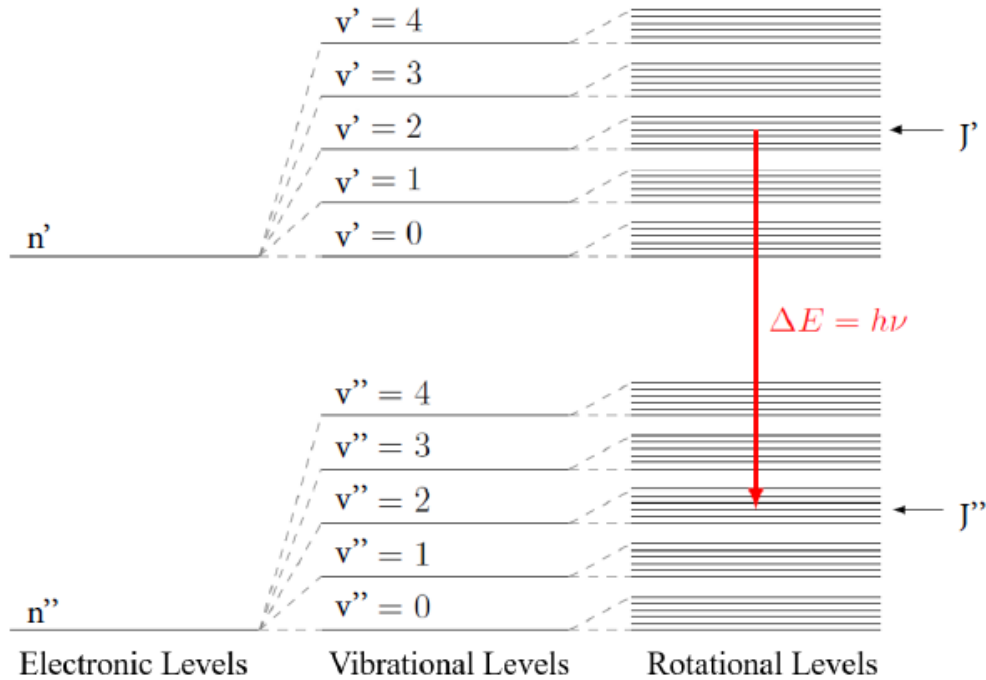
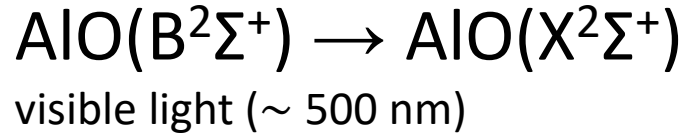
$$\sum_{\text{sub-rot states}} S_{J''}^{J'} = (2 - \delta_{0,\Lambda'}) (2S' + 1) (2J' + 1)$$

Normalisation, Istvan Kovacs (1969)

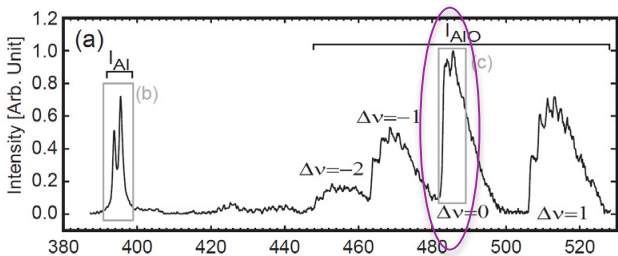
$$N_{n',v',J'} = N_{n'} \cdot \frac{1}{2} \cdot (2J' + 1) \cdot \frac{\exp\left(-\frac{hc \cdot F_{v'}(J')}{k_B \cdot T_{rot}}\right)}{Q_{rot,n',v'}(T_{rot})} \cdot \frac{\exp\left(-\frac{hc \cdot G_{n'}(v')}{k_B \cdot T_{vib}}\right)}{Q_{vib,n'}(T_{vib})}$$

Population density of the excited state

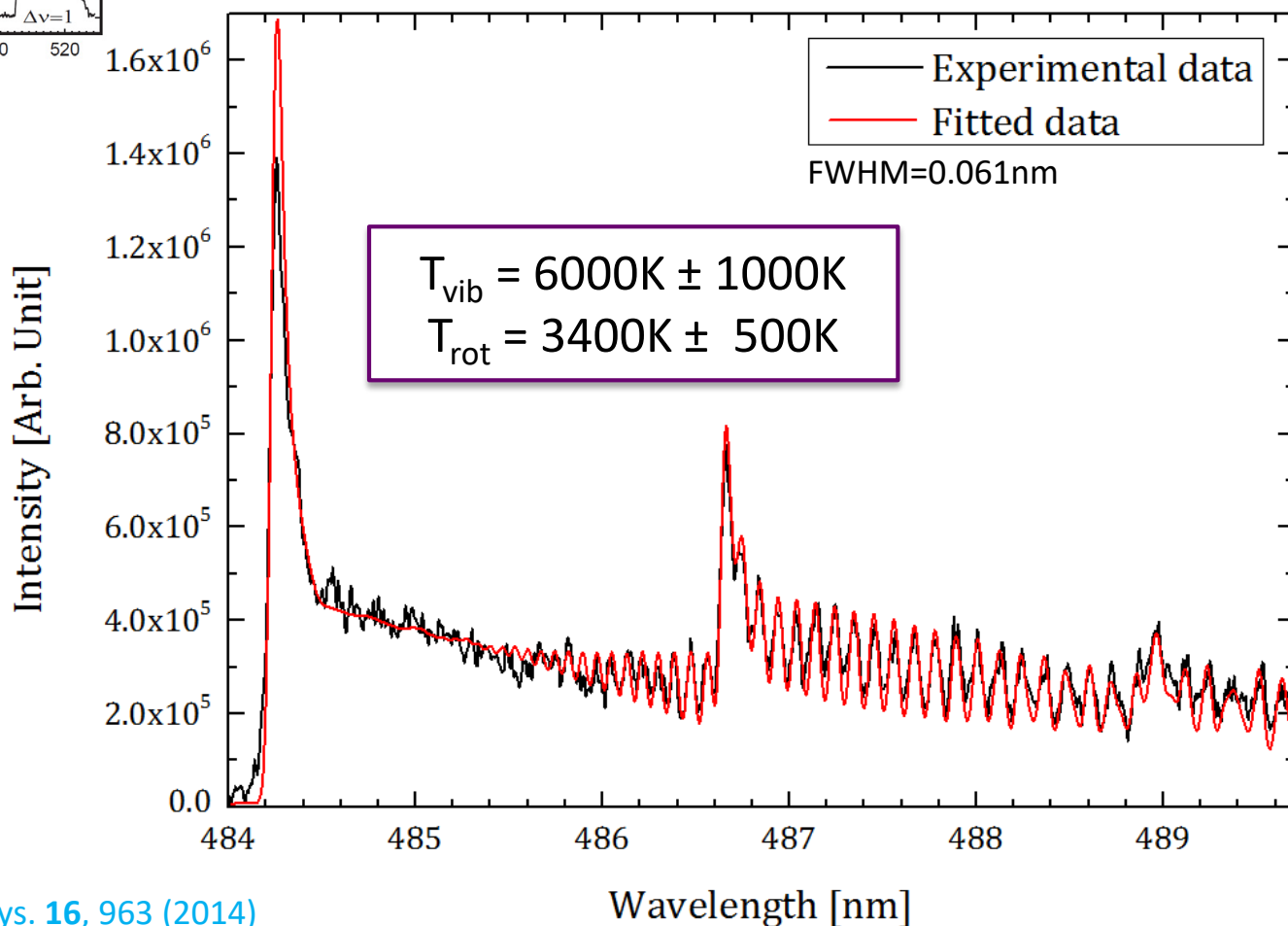


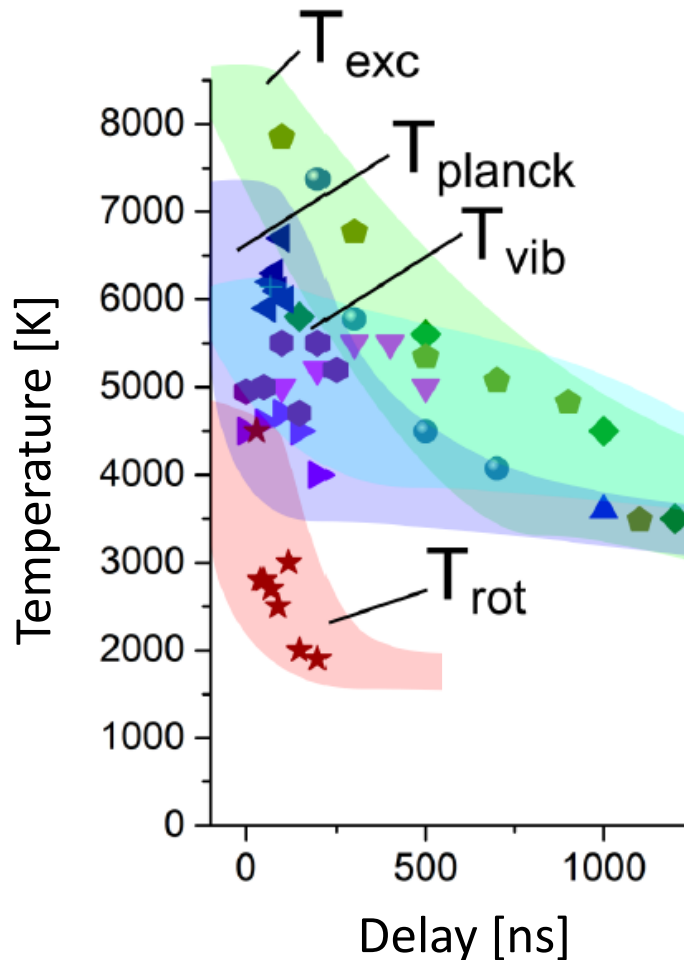


Atomic AlO emission



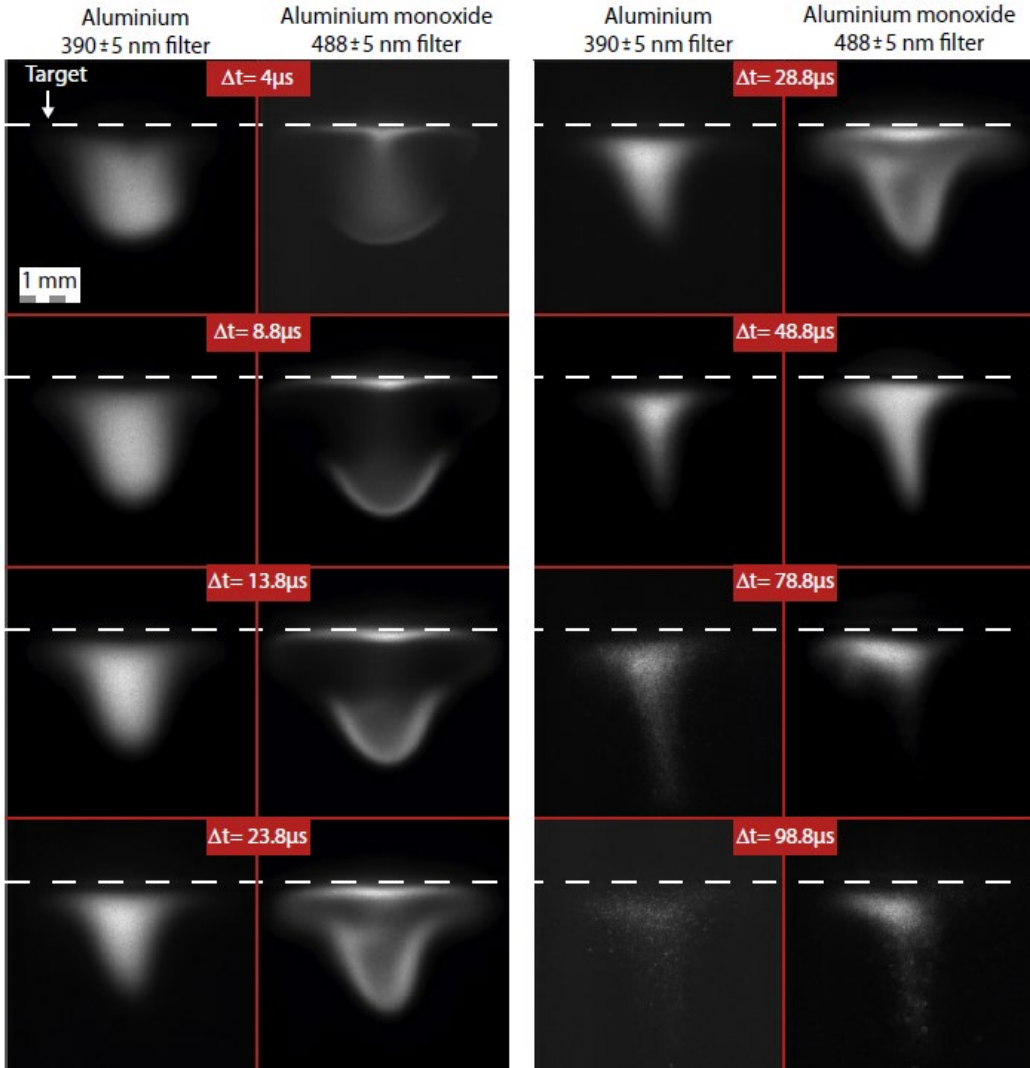
AlO molecules emission





- ▲ b - III - BO -  $T_{planck}$
- ▼ b - IV - Graphite -  $T_{vib}$
- ◆ b - V - Graphite -  $T_{vib}$
- ◀ b - VI - Ti -  $T_{planck}$
- ▶ b - VII - Ti -  $T_{planck}$
- ◉ b - VIII - Cu -  $T_{planck}$
- ★ b - IX - Graphite -  $T_{rot}$
- ⬠ b - X - Ti -  $T_{exc}$
- b - XI - Cu -  $T_{exc}$

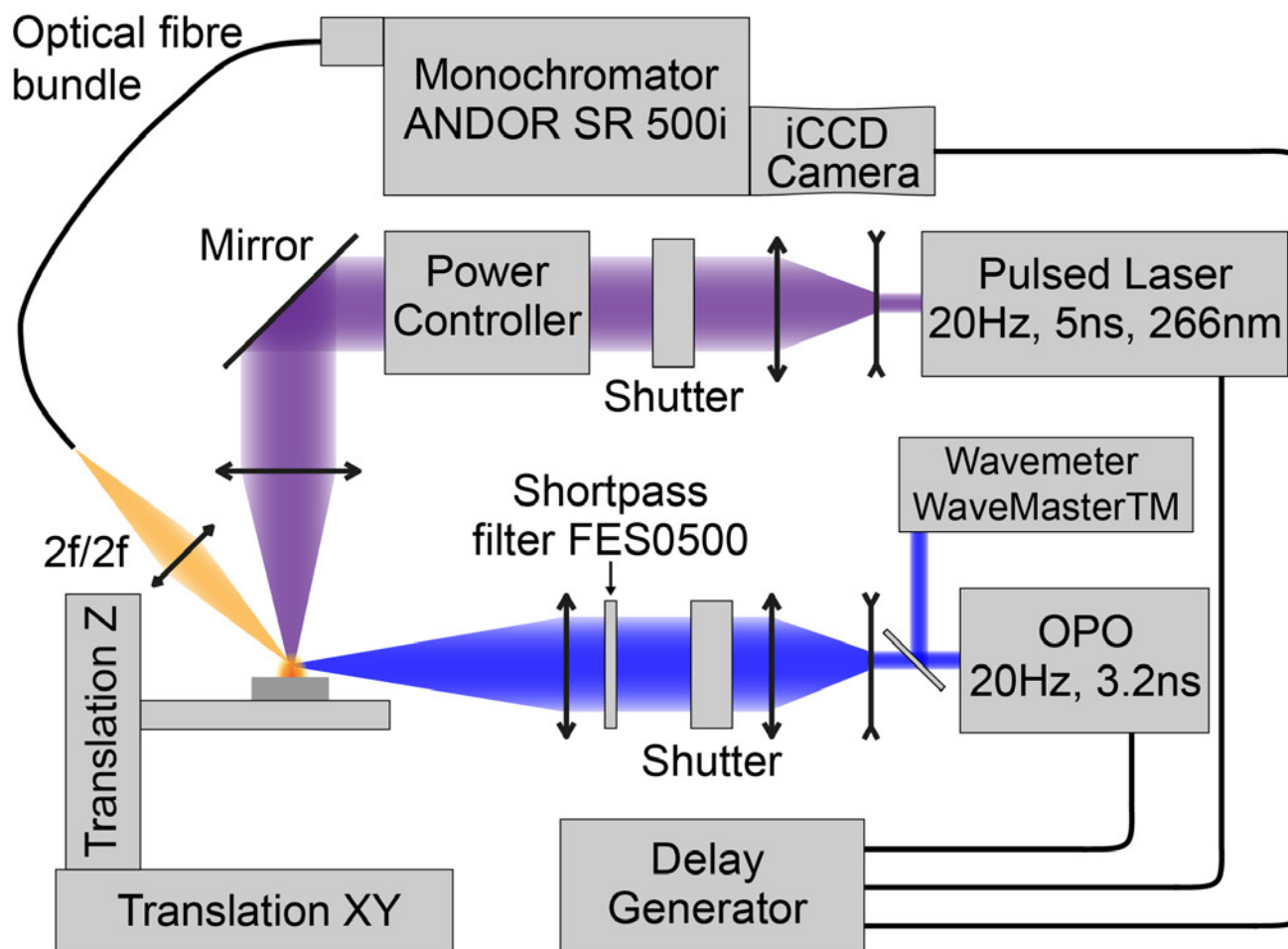
**Fast cooling, but  
what are we really  
measuring ?**

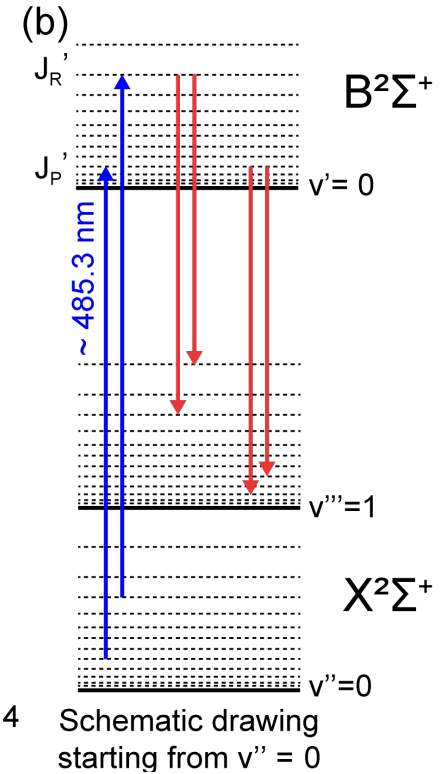
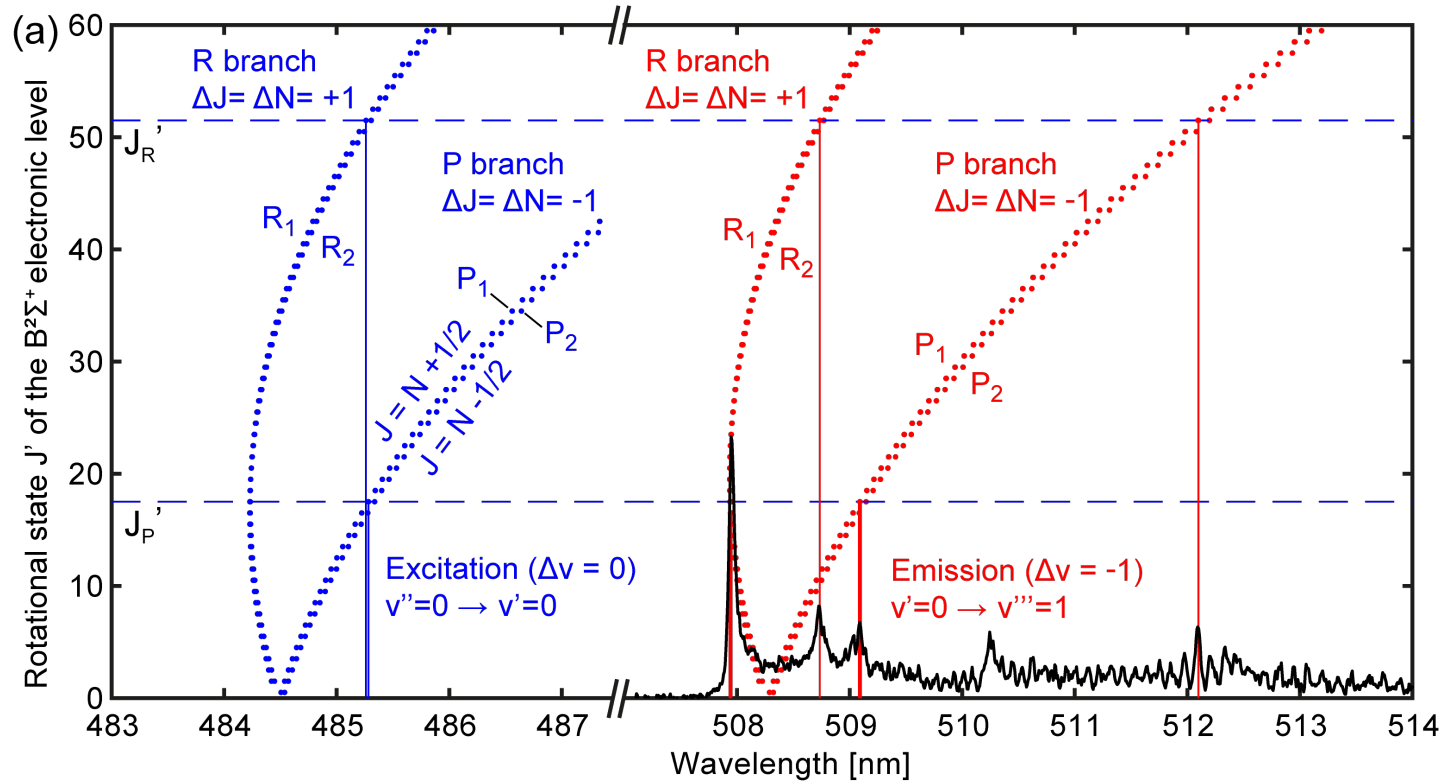


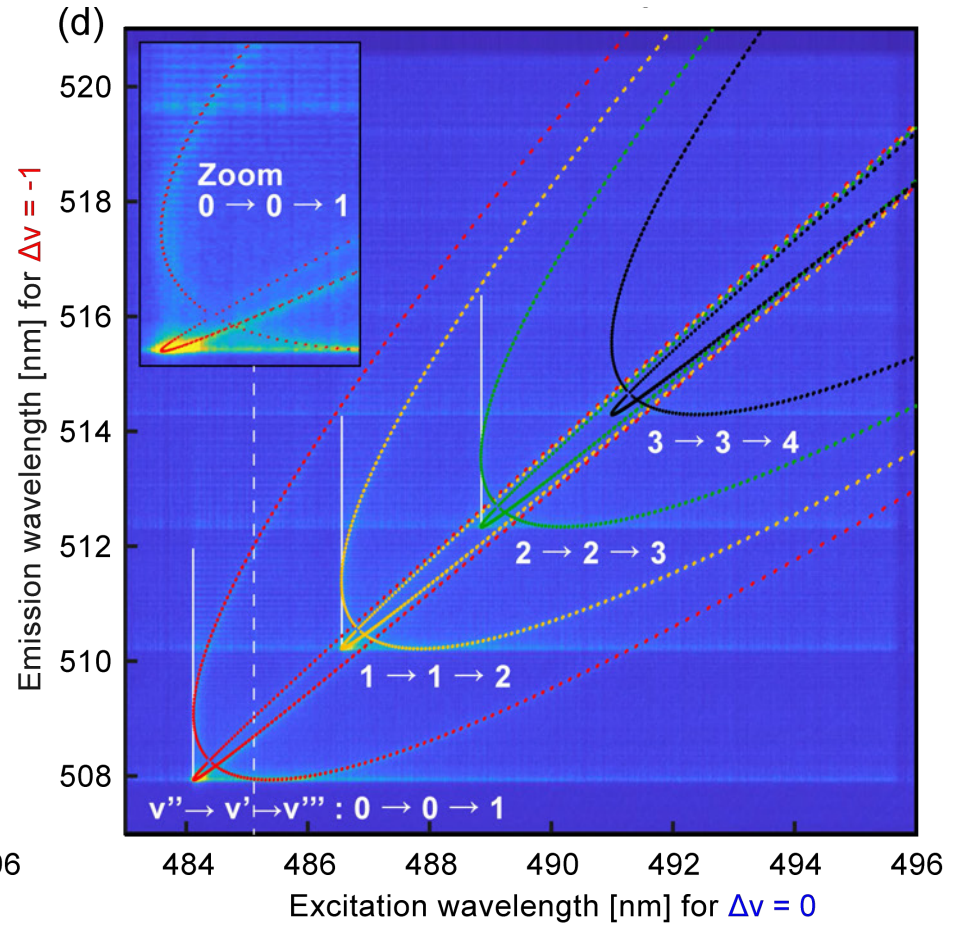
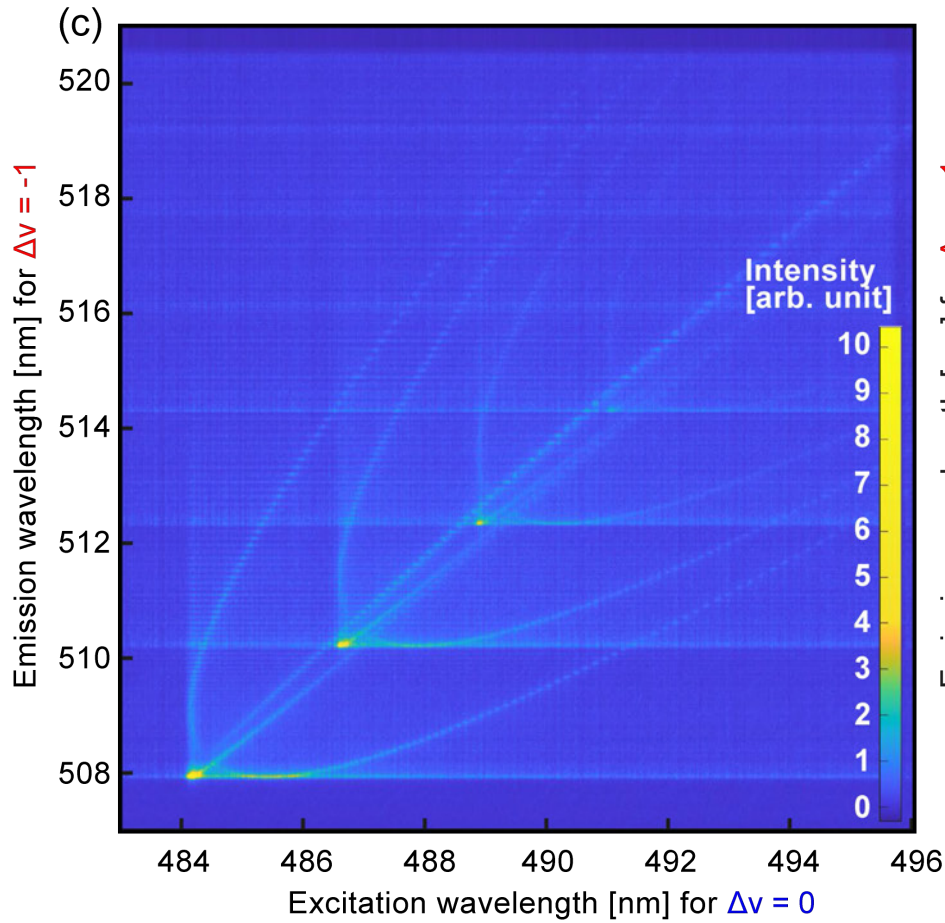
What are we really measuring ?

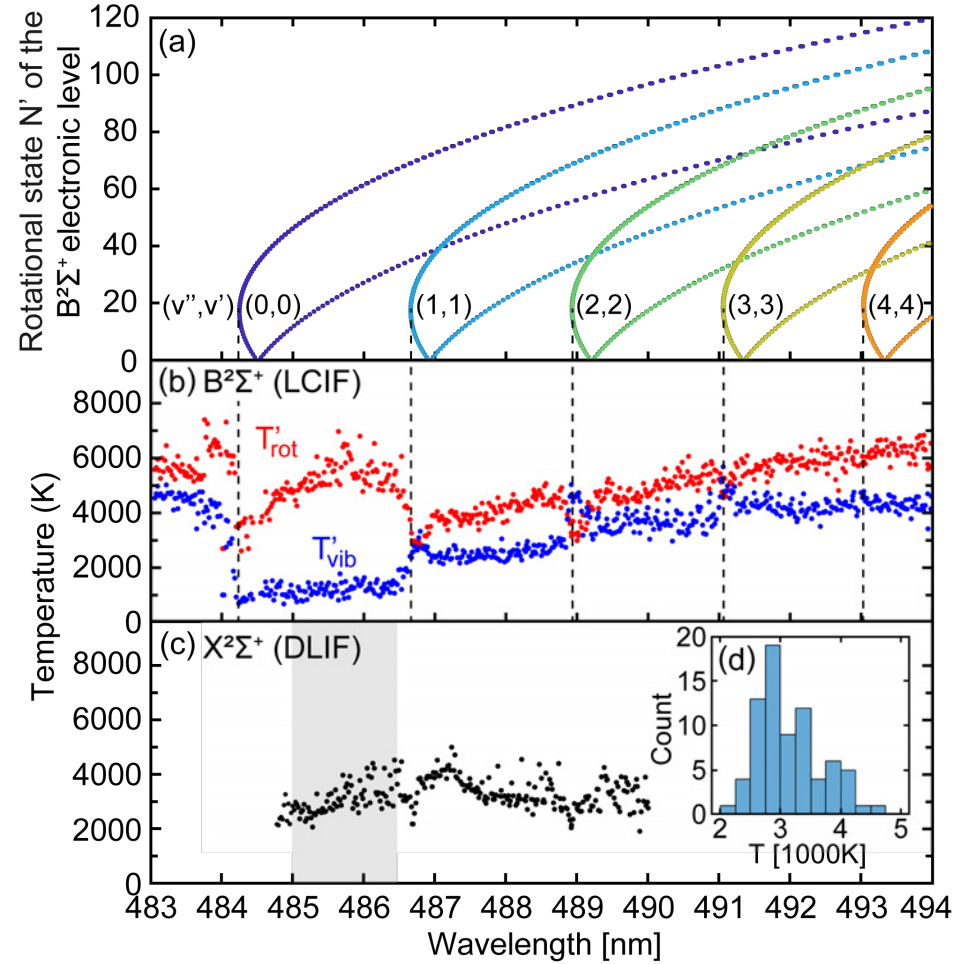
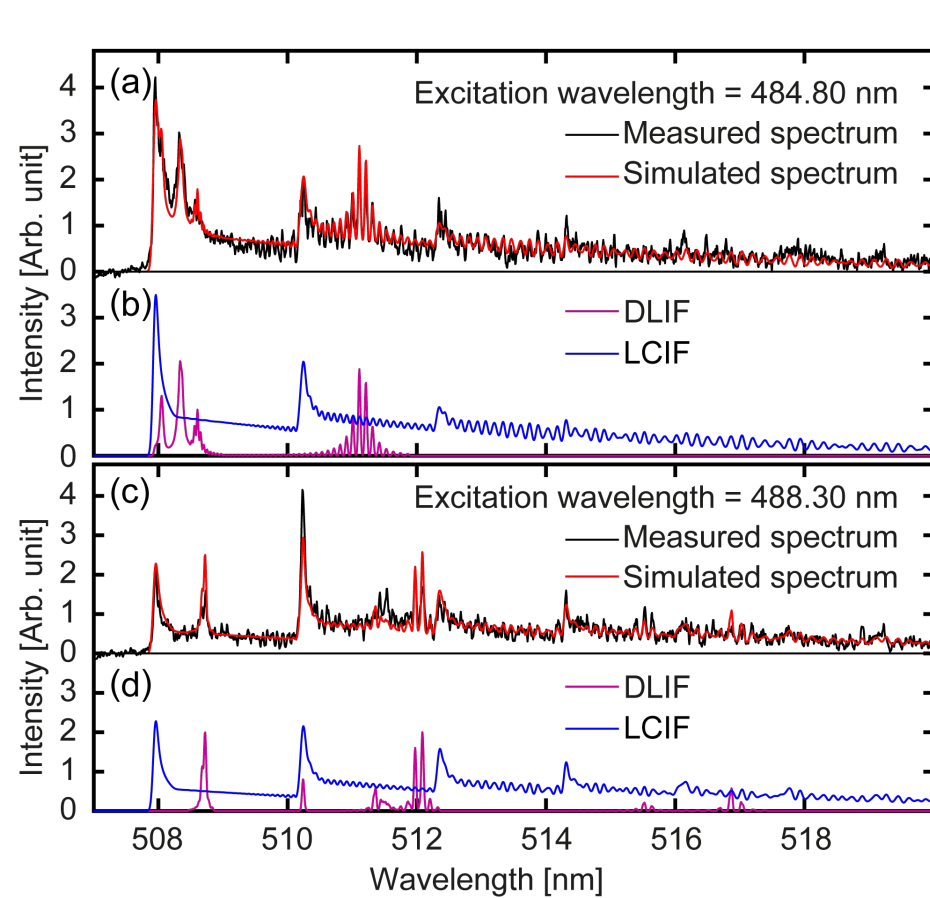
Emission from “newly” produced molecules ?





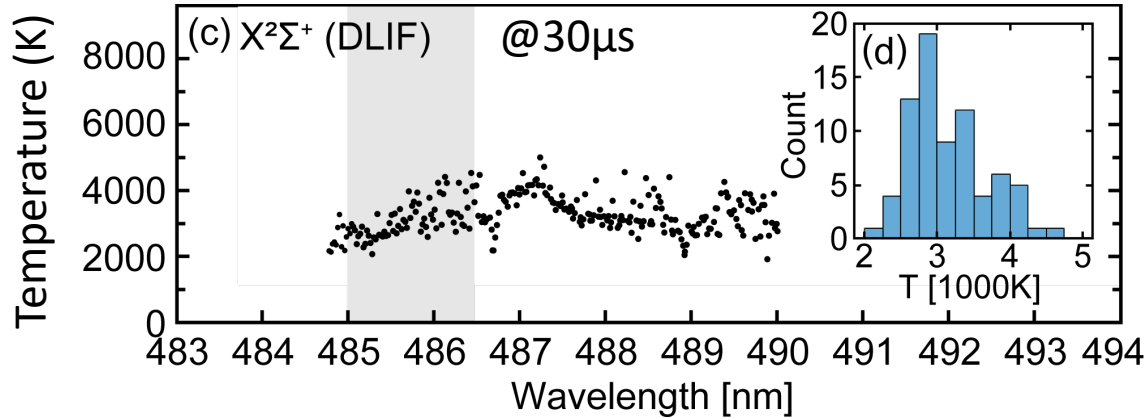






Collisionally induced fluorescence contribution in blue (LCIF)  
Direct fluorescence contribution in magenta (DLIF)





## LIF

@30 $\mu$ s :  $T_{X^2\Sigma^+} = 3150$  K (SD = 552 K)

Temperature interval for a confidence level of 70% (two-sided) is  $\pm 67$  K.

@5 $\mu$ s :  $T_{X^2\Sigma^+} = 3700$  K (SD = 5302 K)

Temperature interval for a confidence level of 70% (two-sided) is  $\pm 64$  K.

## Plasma emission

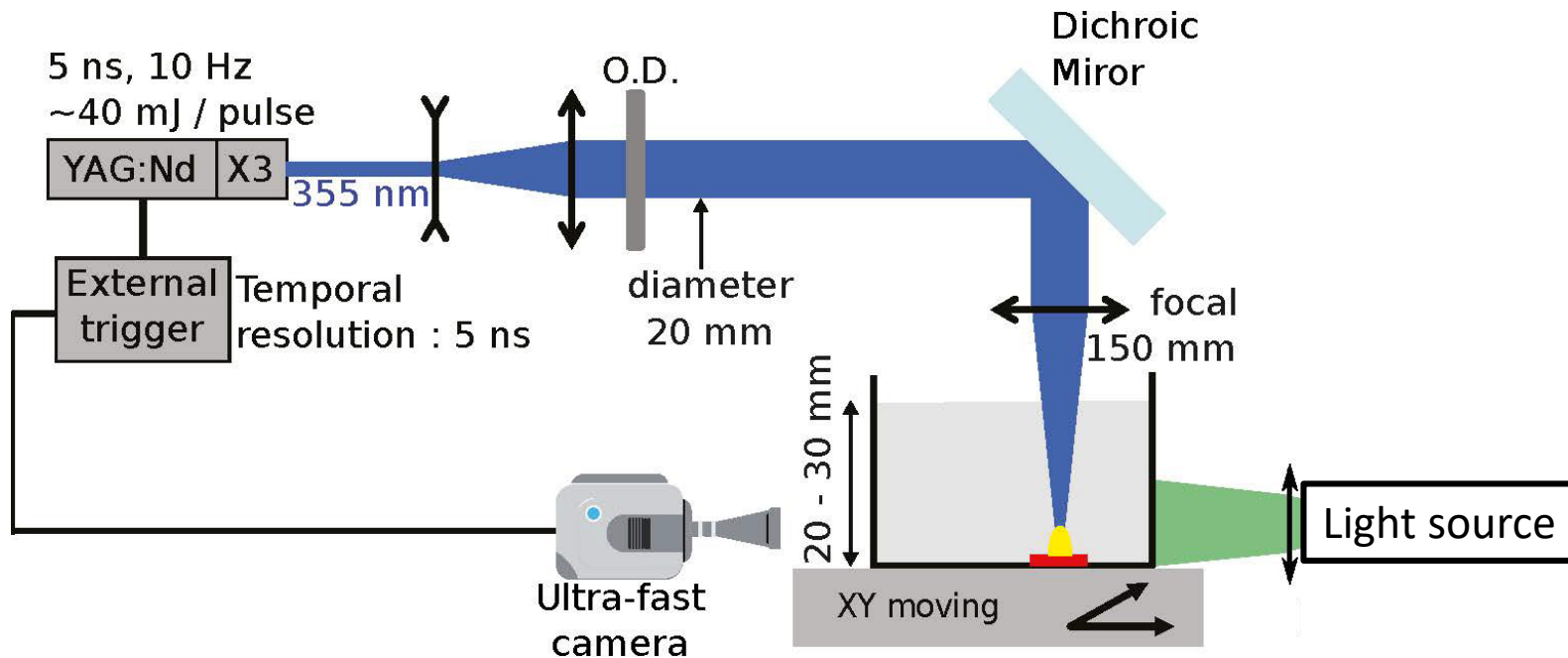
$$T_{B^2\Sigma^+}^{rot} = 3130 \pm 100 \text{ K (70\%).}$$

Vs.

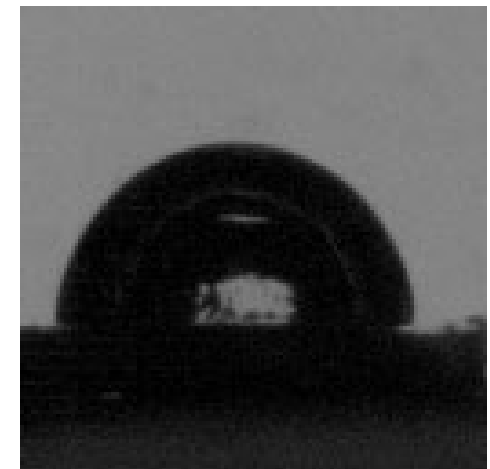
$$T_{B^2\Sigma^+}^{rot} = 3850 \pm 100 \text{ K (70\%)}$$

## Bubble dynamics

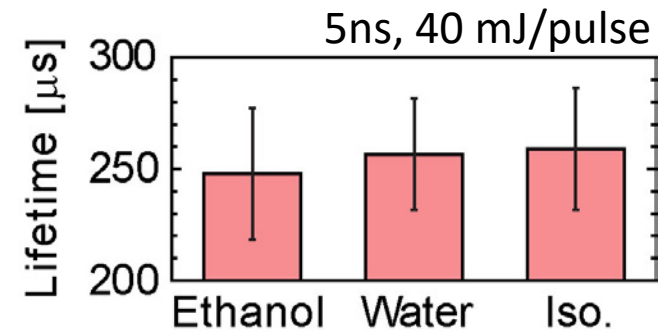
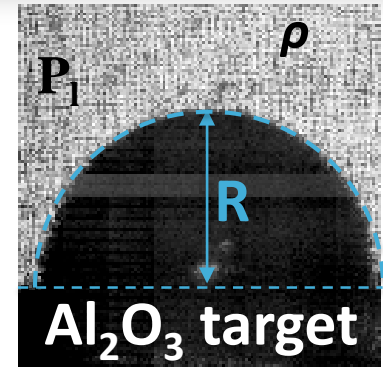
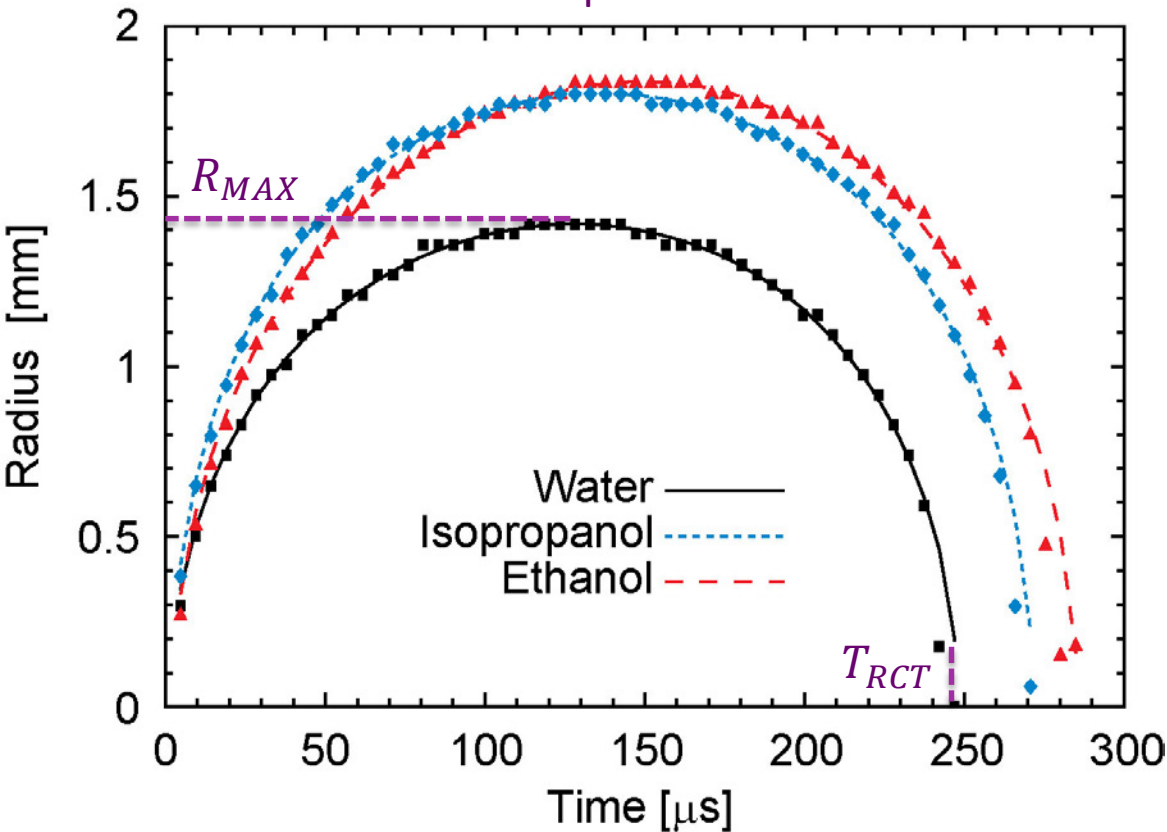
- **Imaging of laser-generated bubbles in solvents of low viscosity**
- **Rayleigh-Plesset equation**
- **Gilmore model**
- **Bubbles in highly viscous liquids**



Camera Phantom v711 from  
Vision Research  
Zoom 6000 from Navitar  
Frame rate 210000 fps



Let me focus on the first oscillation.  
The bubble radius appears symmetric  
with respect to time !



Rayleigh collapse time:

$$T_{RCT} = 1,83 R_{MAX} \sqrt{\frac{\rho}{P_l}}$$



## Rayleigh-Plesset (RP) equation

Derive from Navier–Stokes equations in spherical coordinates, assuming a Newtonian fluid, **incompressible**

$$R\ddot{R} + \frac{3}{2}\dot{R}^2 = \frac{1}{\rho} \left[ P_B(t) - P_l - \frac{2\sigma}{R} - \frac{4\eta\dot{R}}{R} \right]$$

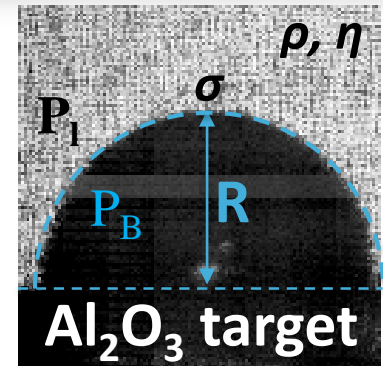
Relative contribution of each term :

$$R \approx 1 \text{ mm}, t \approx 300 \mu\text{s}, \sigma_w \approx 0,1 \text{ N/m}, \rho_w \approx 1 \text{ g/cm}^3, \eta_w \approx 10^{-3} \text{ Pa}\cdot\text{s}$$

$$\text{Weber number } We = \rho \dot{R}^2 R / \sigma \simeq 1 \times 10^2$$

$$\text{Reynolds number } Re = \rho \dot{R} R / \eta \simeq 3 \times 10^3$$

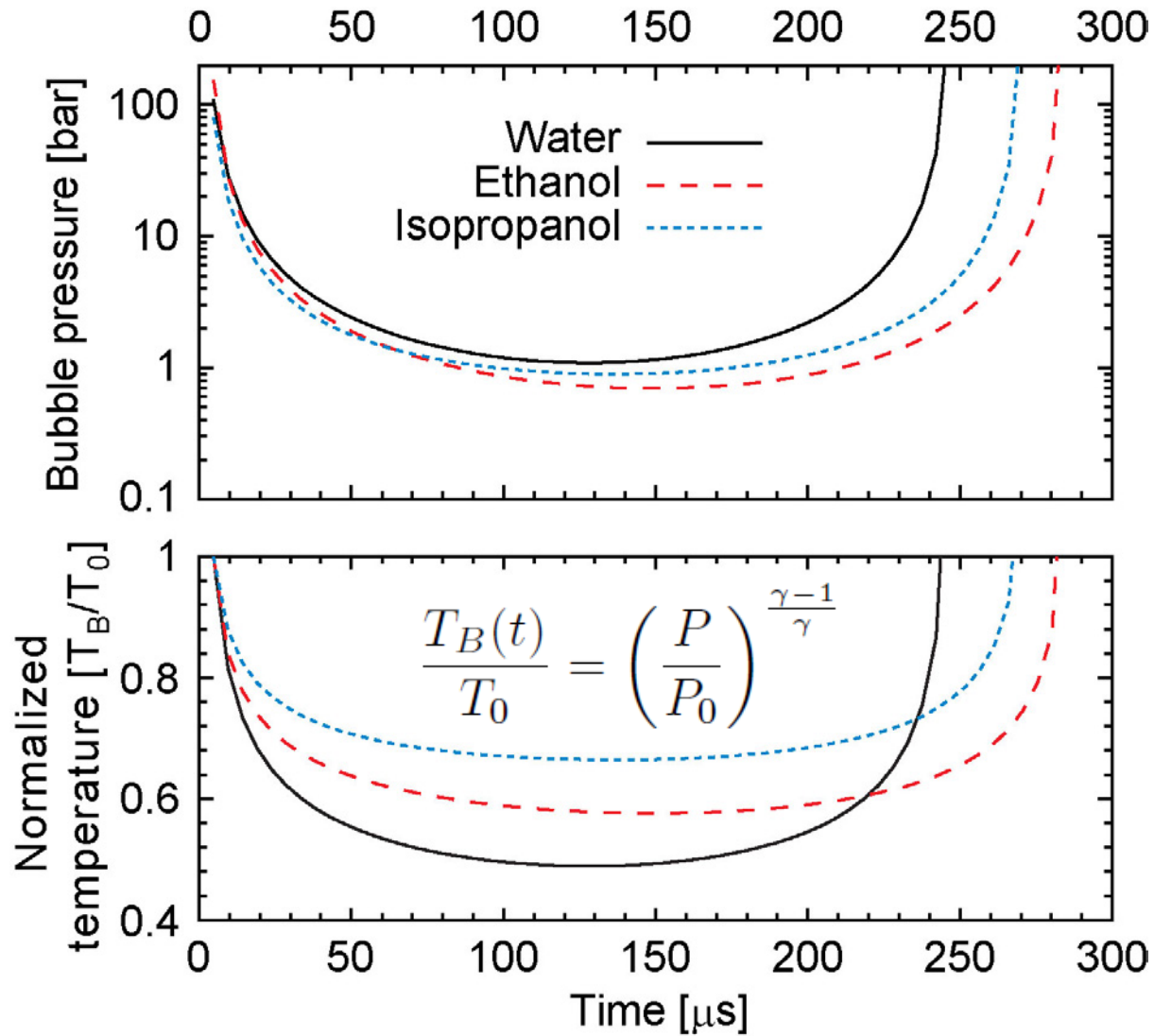
The surface motion of the bubble is driven by inertial forces



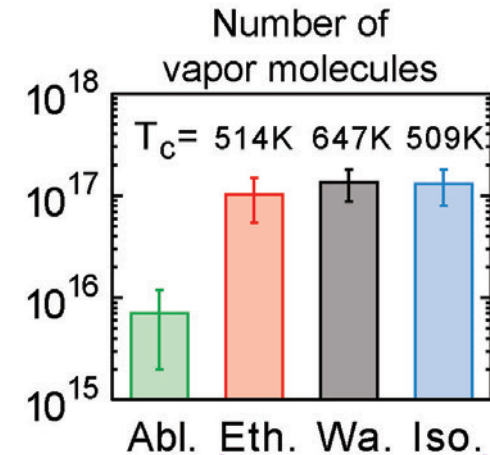
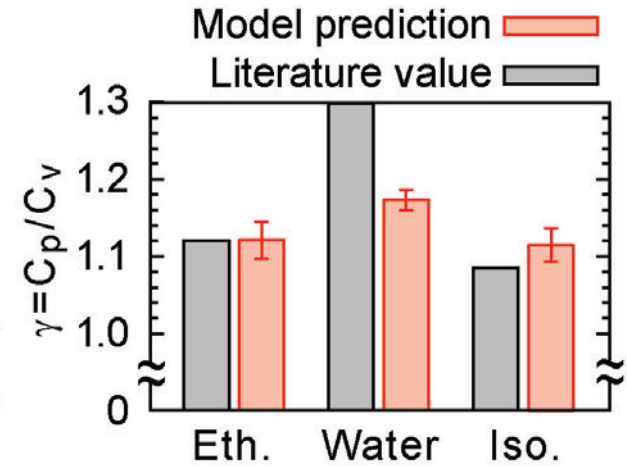
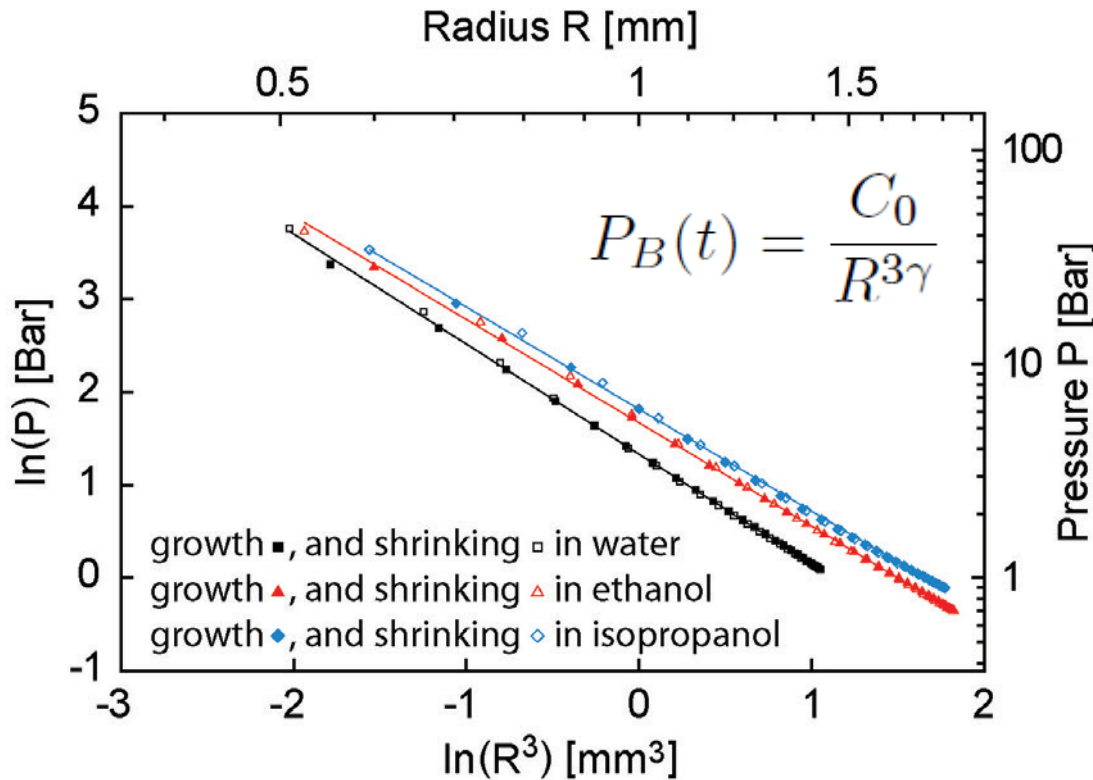
$\sigma$  fluid surface tension  
 $\rho$  liquid mass density  
 $\eta$  dynamic viscosity

Simplified Rayleigh-Plesset (RP) equation for **purely inertial dynamics**

$$\rho \left( R\ddot{R} + \frac{3}{2}\dot{R}^2 \right) = P_B(t) - P_l$$



Isentropic process !



Vapor mainly composed of solvent molecules (25% pulse energy)

Adiabatic ?

$R \approx 1 \text{ mm}$ ,  $h \approx 100 \text{ W/m}^2/\text{K}$ ,  $T_c \approx 650 \text{ K}$

$\Phi = h\Delta T(\pi R^2 + 2\pi R^2) \approx 0,33 \text{ W}$

300  $\mu\text{s}$  → 0,1 mJ

But the Rayleigh-Plesset (RP) model can't explain the damping of the bubble oscillation ... we need to account the compressibility → Gilmore model

Computes:  $R(t)$ ,  $P_B(t)$  and the pressure distribution in the surrounding liquid.

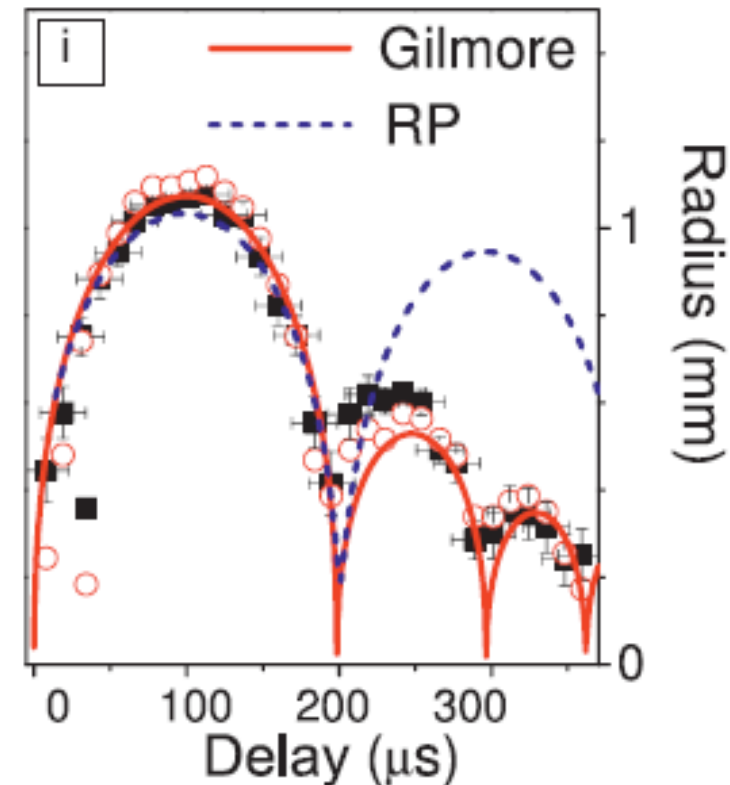
Considers: liquid compressibility, viscosity and surface tension.

Assumes: a constant gas content of the bubble, neglecting evaporation, condensation, gas diffusion through the bubble wall, and heat conduction.

*Gas content variation during the collapse is arbitrary added*

State equation: Tait's equation

$$\frac{P+B}{p_\infty+B} = \left(\frac{\rho}{\rho_0}\right)^n \quad \text{Water: } B = 314 \text{ MPa, } n=7$$



S. Barcikowski et al., MRS BULLETIN 44, 382 (2019)



But the Rayleigh-Plesset (RP) model can't explain the damping of the bubble oscillation ...  
we need to account the compressibility → Gilmore model

$$\dot{U} = \left[ -\frac{3}{2} \left( 1 - \frac{U}{3C} \right) U^2 + \left( 1 + \frac{U}{C} \right) H + \frac{U}{C} \left( 1 - \frac{U}{C} \right) R \frac{dH}{dR} \right] \cdot \left[ R \left( 1 - \frac{U}{C} \right) \right]^{-1}$$

$R$  bubble radius,  $U = dR/dt$  is the bubble wall velocity,  
 $C$  speed of sound in the liquid at the bubble wall,  
 $H$  enthalpy difference between the liquid at pressure  $P(R)$  at the bubble wall and at hydrostatic pressure  $p_\infty$

$$H = \int_{p_\infty}^{P(R)} \frac{dp}{\rho} \quad p \text{ and } \rho \text{ are the pressure and the density within the liquid}$$

The pressure  $P$  at the bubble wall is given by

$$P = \left( p_\infty + \frac{2\sigma}{R_n} \right) \left( \frac{R_n}{R} \right)^{3\kappa} - \frac{2\sigma}{R} - \frac{4\mu}{R} U$$

$\kappa$  the ratio of the specific heat  
 $P$  is uniform in the bubble.  
 $R_n$  equilibrium radius ( $P = P_{hydro}$ )  
 $R_n$  "measure" of the gas content

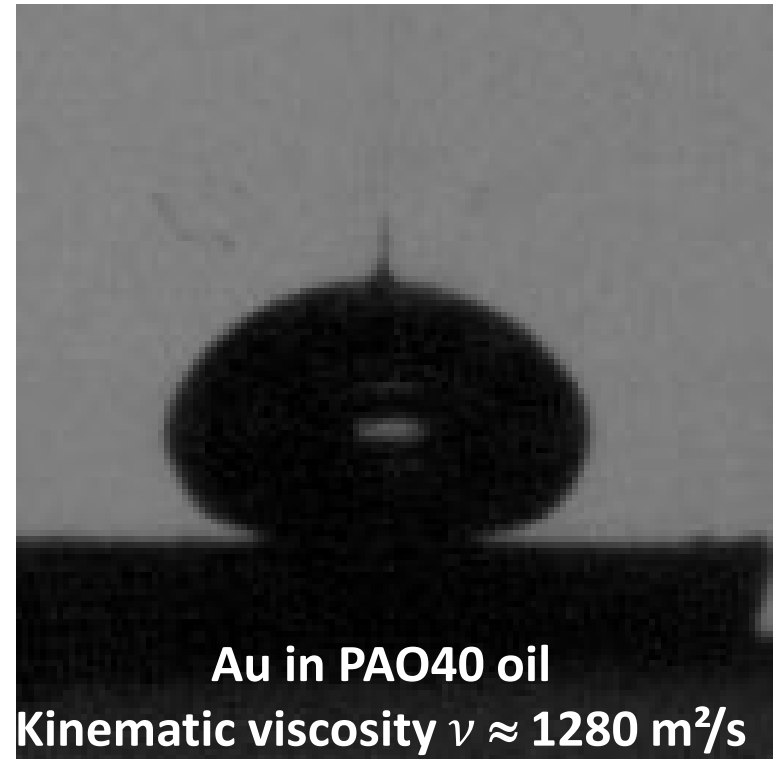
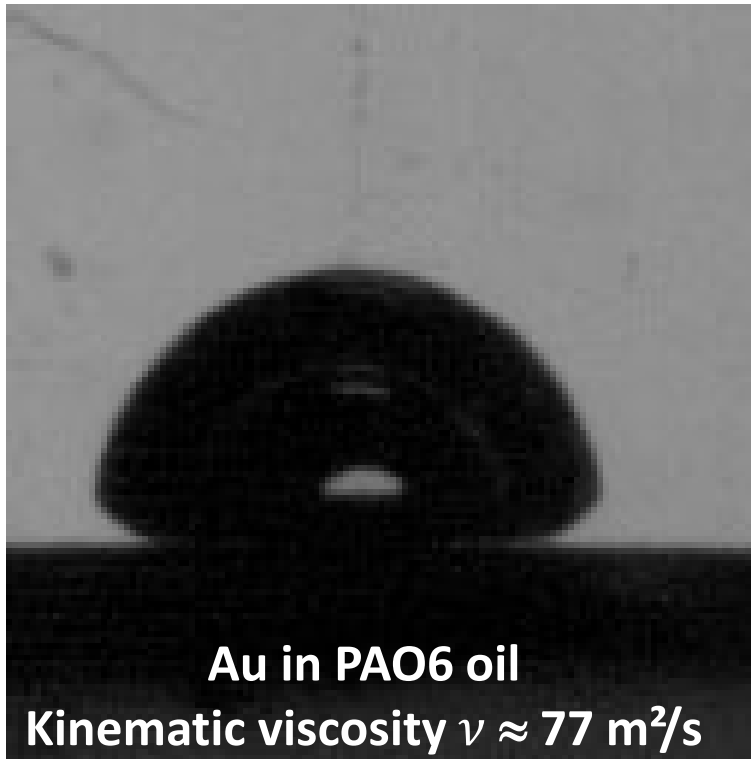
$$C = (c_0^2 + (n-1)H)^{1/2},$$

Assuming Tait's equation



$$H = \frac{n(p_\infty + B)}{(n-1)\rho_0} \left[ \left( \frac{P+B}{p_\infty+B} \right)^{(n-1)/n} - 1 \right]$$

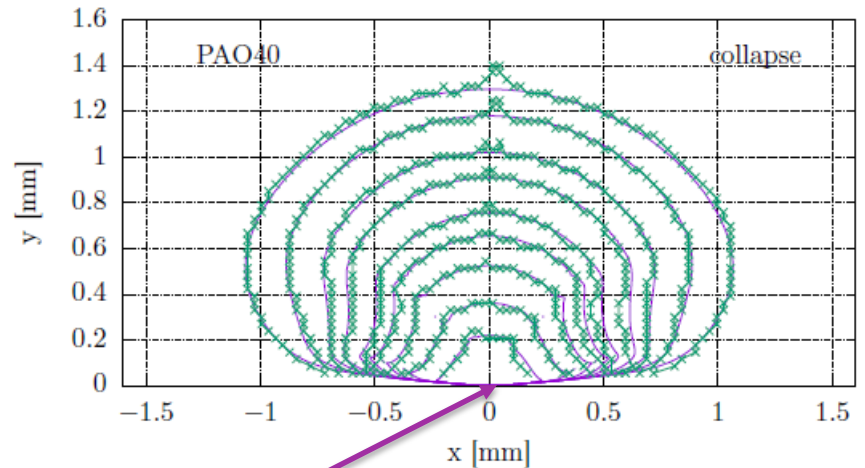
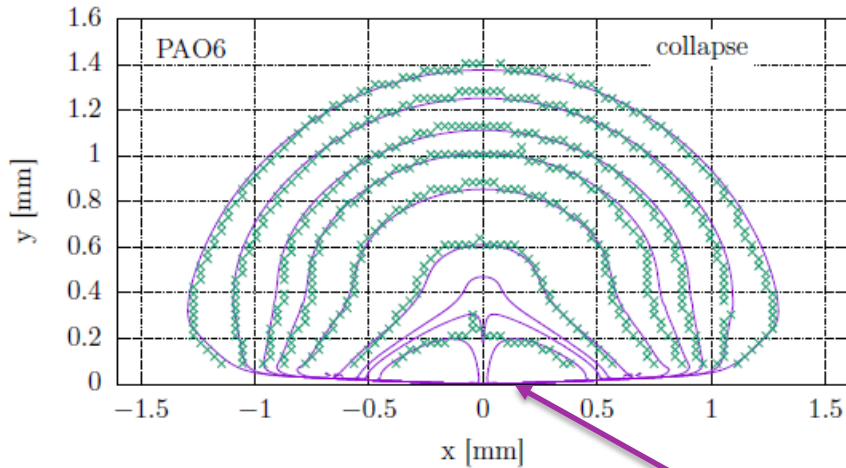
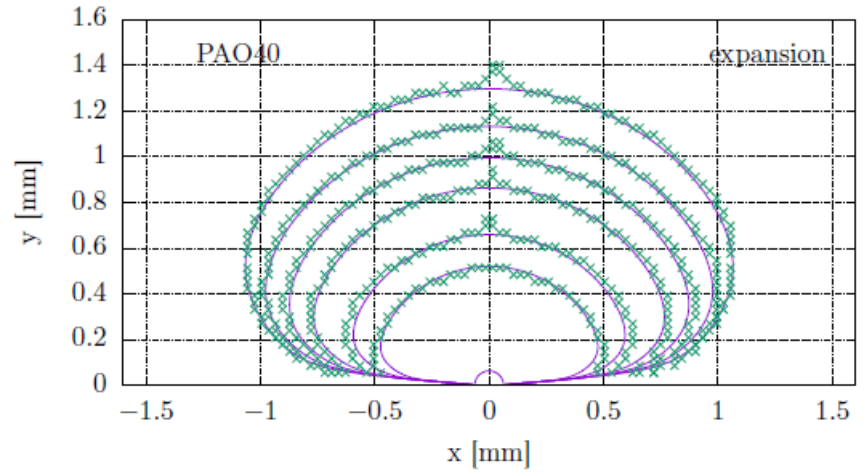
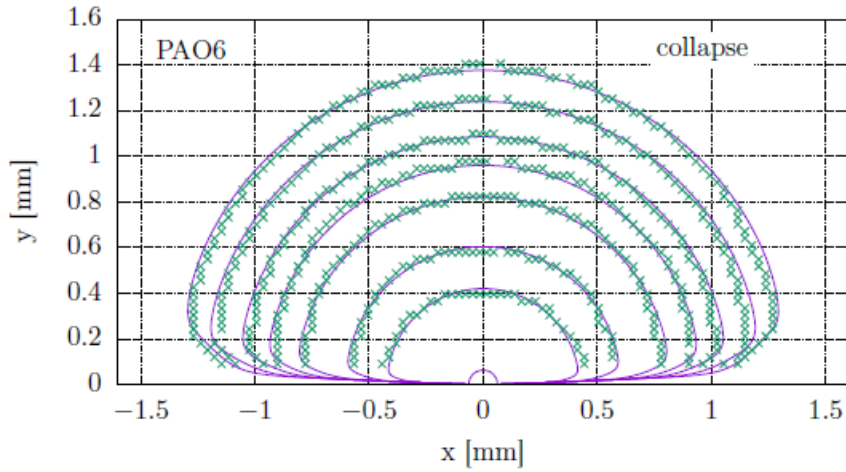
Ablation in viscous liquids : poly-*alpha*-olefin (PAO)



Huge capillary number  $C_a = \frac{\rho \nu V_{cl}}{\sigma} > 100$ , the contribution of the viscous forces to the friction drastically increases. The Rayleigh-Plesset and Gilmore are no more appropriate

Direct resolution of the continuity and Navier-Stokes equations

(Finite volume method, *OpenFOAM* open source software @ <https://www.openfoam.com/>)



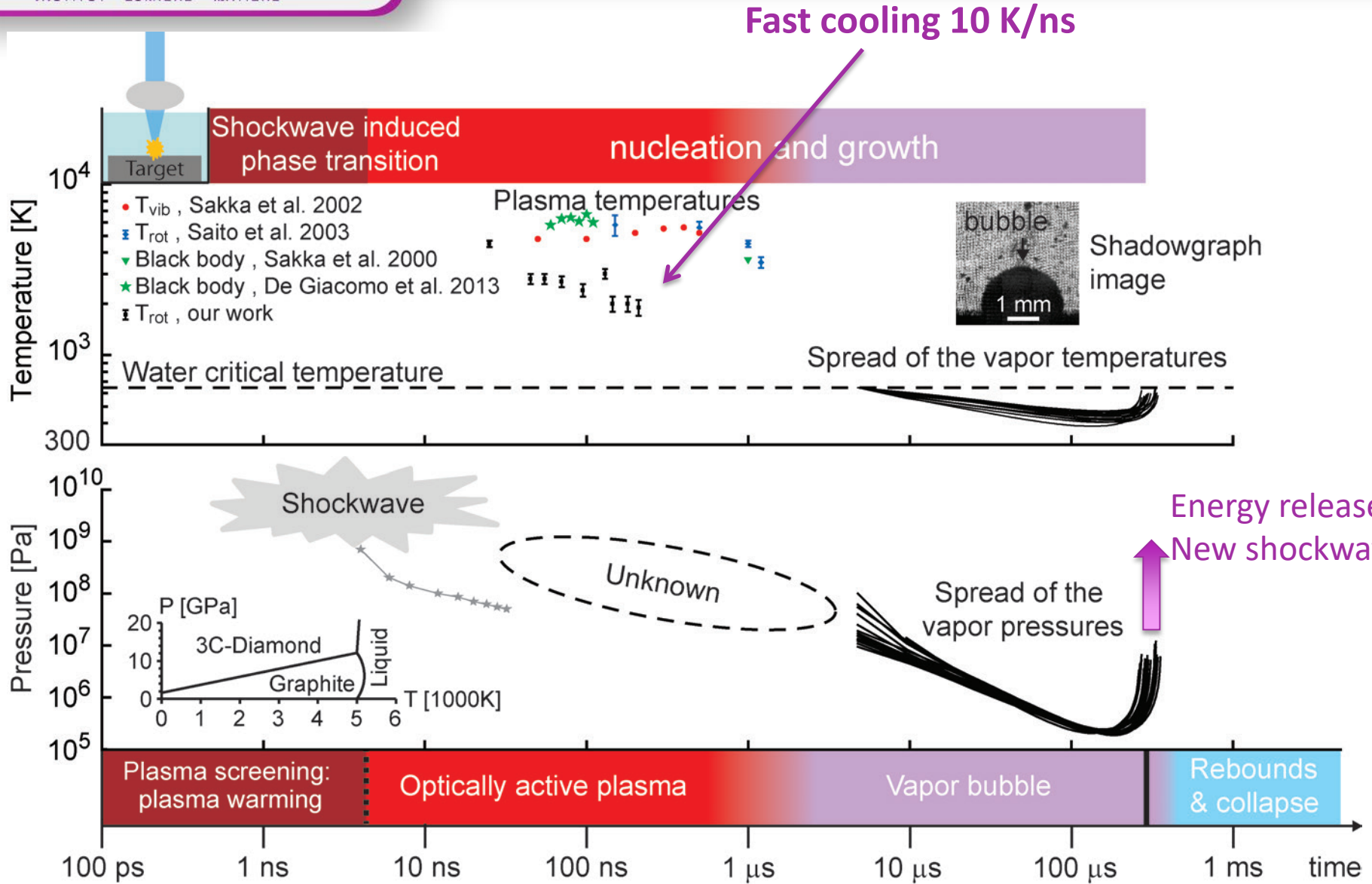
Suppression of the jet



Collaboration with  
C. Lechner @ TU Wien

# Conclusion





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**PhD students:** **Julien Lam, Mouhamed Diouf, Gaetan Laurens, Arsène Chemin**