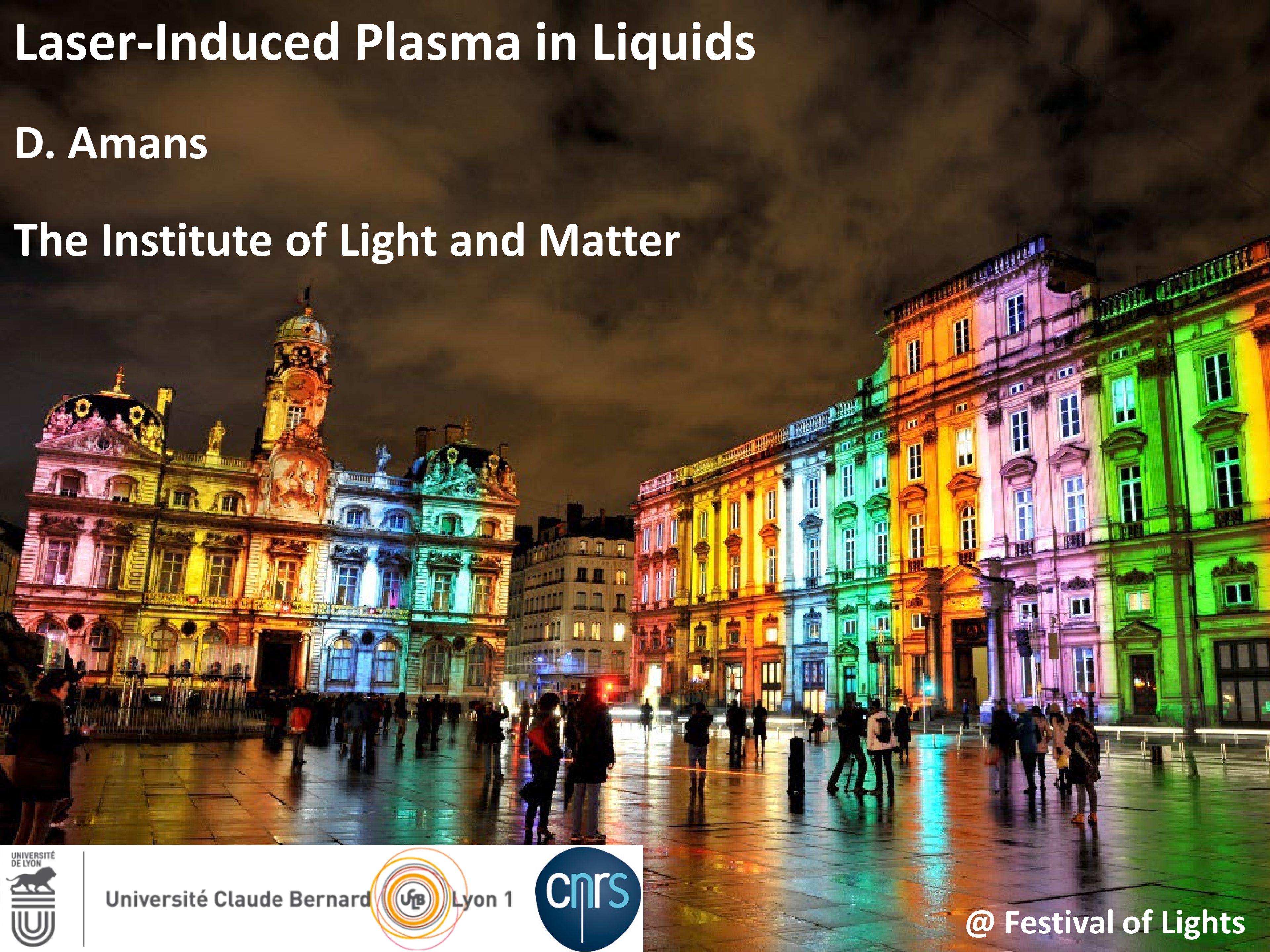
Laser-Induced Plasma in Liquids

D. Amans

The Institute of Light and Matter



@ Festival of Lights

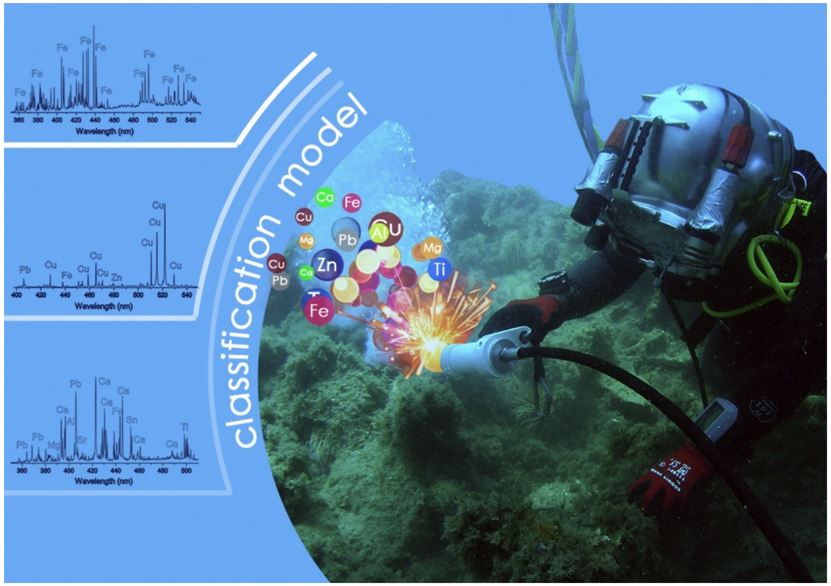
UNIVERSITÉ DE LYON

Université Claude Bernard Lyon 1

cnrs

Laser ablation in liquids attracts a broad interest

LIBS underwater



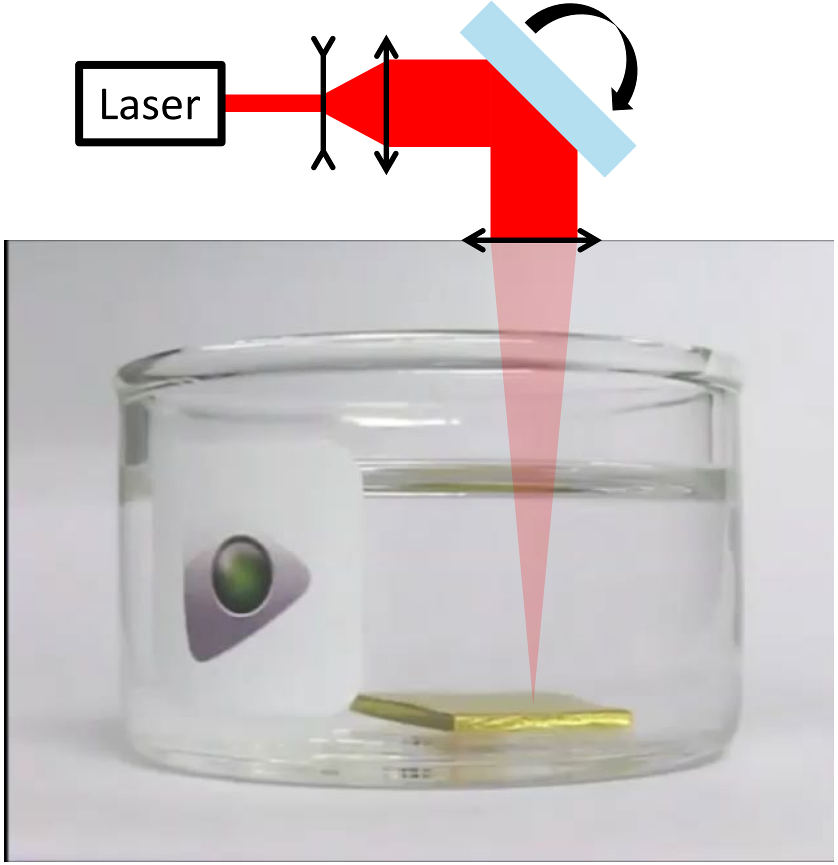
Interest: Geological exploration (oil industry)
Recognition of archeological materials…

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

Laser generation of colloids

fs, ps, ns
10^{10} - 10^{12} W/cm^2

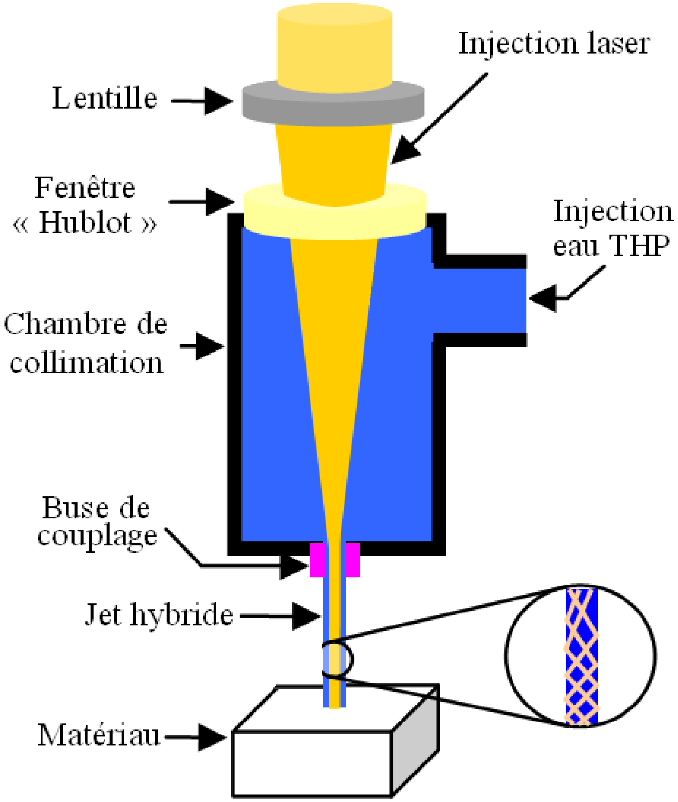
Interest: one step process, particles with surface free of ligands, versatile…



@ Particular GmbH

Laser ablation in liquids attracts a broad interest

Microfabrication

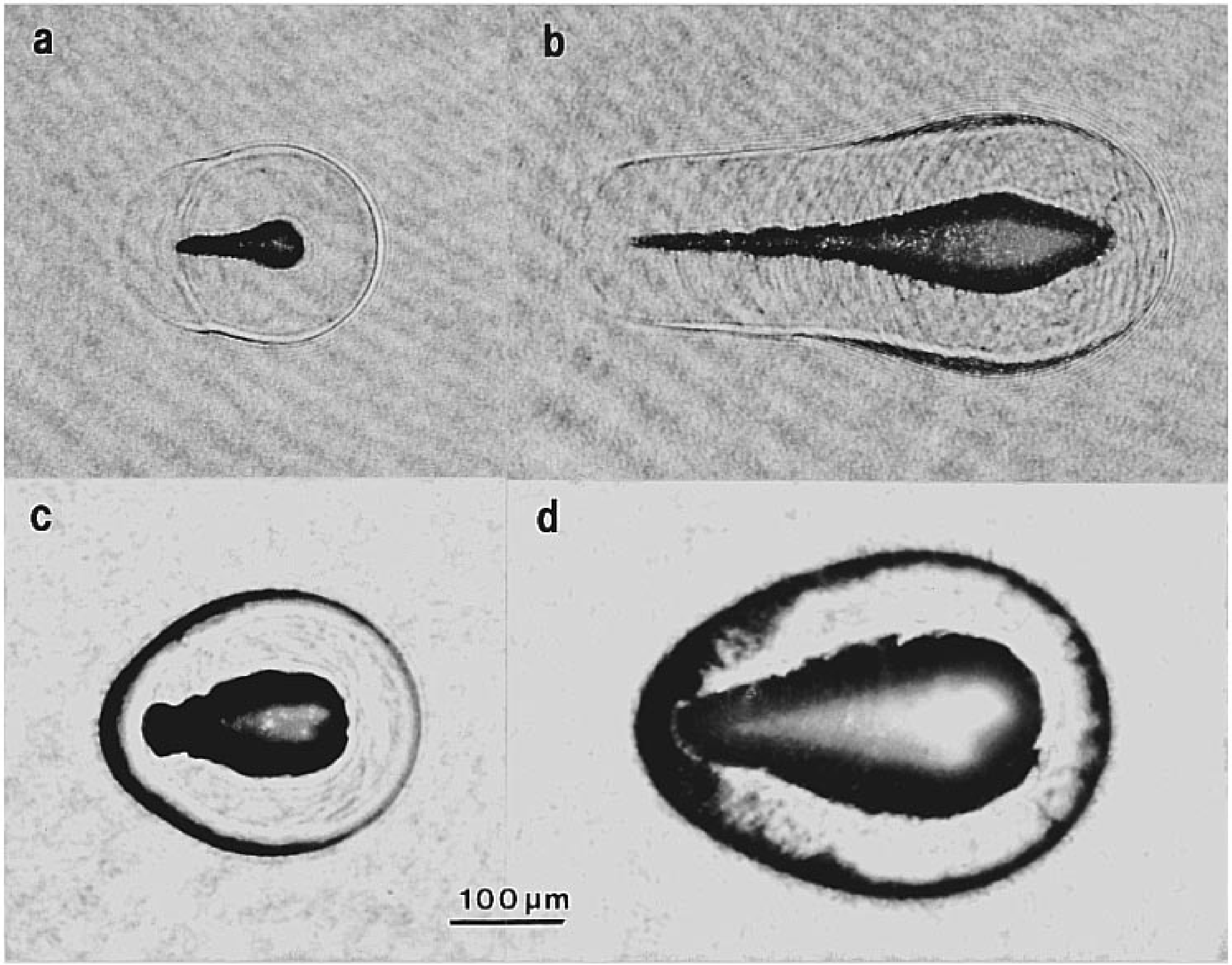


Thèse de Laurent Weiss, *Contribution au développement d'un procédé de découpe laser haute-énergie/ jet d'eau haute-pression couplés. Application à la découpe d'alliages métalliques*. Univ. Lorraine 5 juillet 2013

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

Laser-induced breakdown in liquids

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:

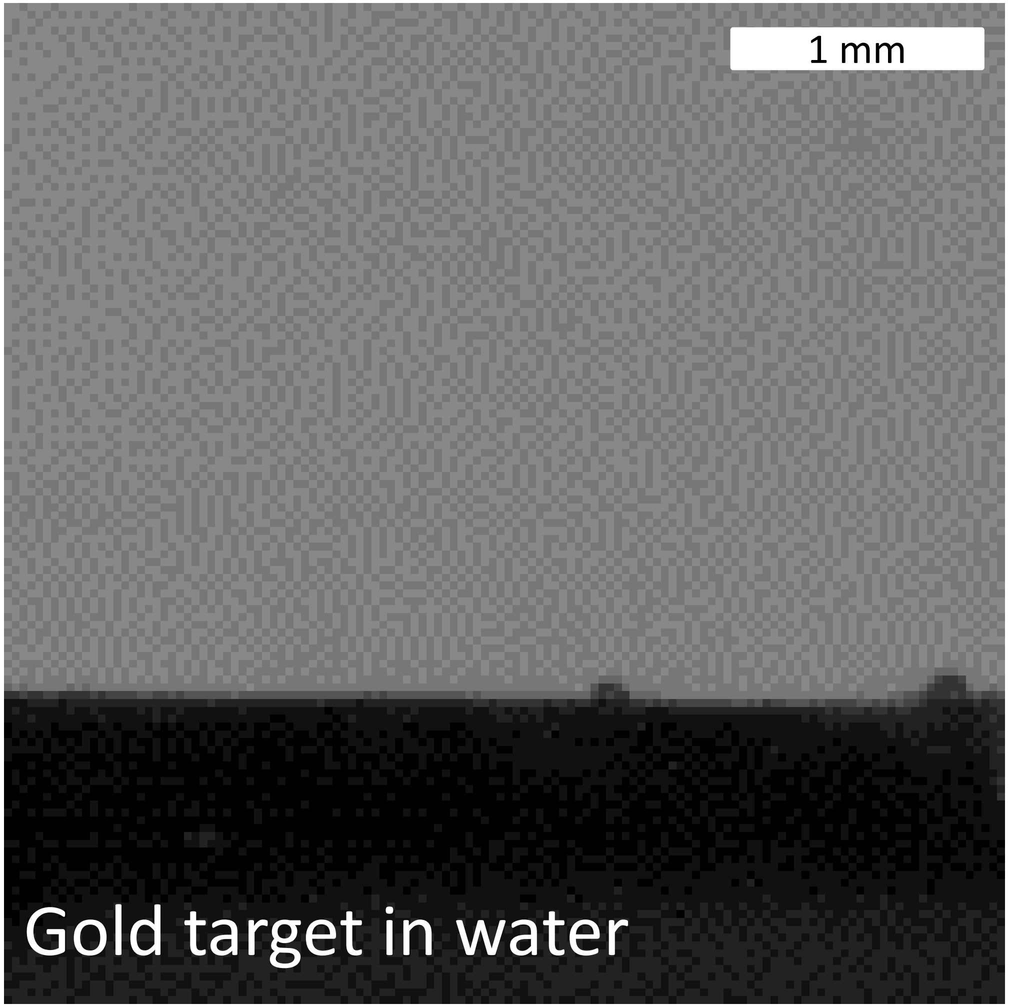
(a) 30 ps, 50 µJ;
(b) 30 ps, 1 mJ;
(c) 6 ns, 1 mJ;
(d) 6 ns, 10 mJ.

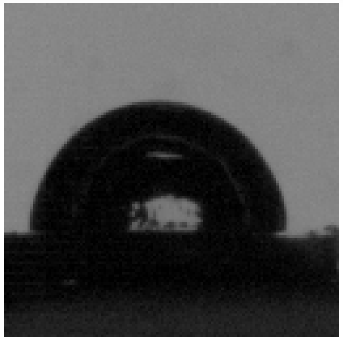
All pictures were taken **44 ns** after the optical breakdown.

A. Vogel, S. Busch, U. Parlitz, *Shock wave emission and cavitation bubble generation by picosecond and nanosecond optical breakdown in water*, J. Acoust. Soc. Am. 100, 148 (1996).

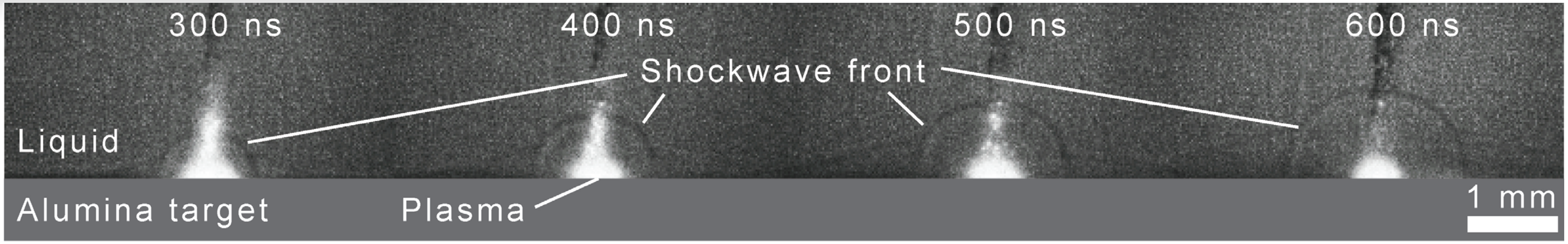
Laser ablation in liquids

Shadowgraph imaging using a fast camera (210 000 fps)

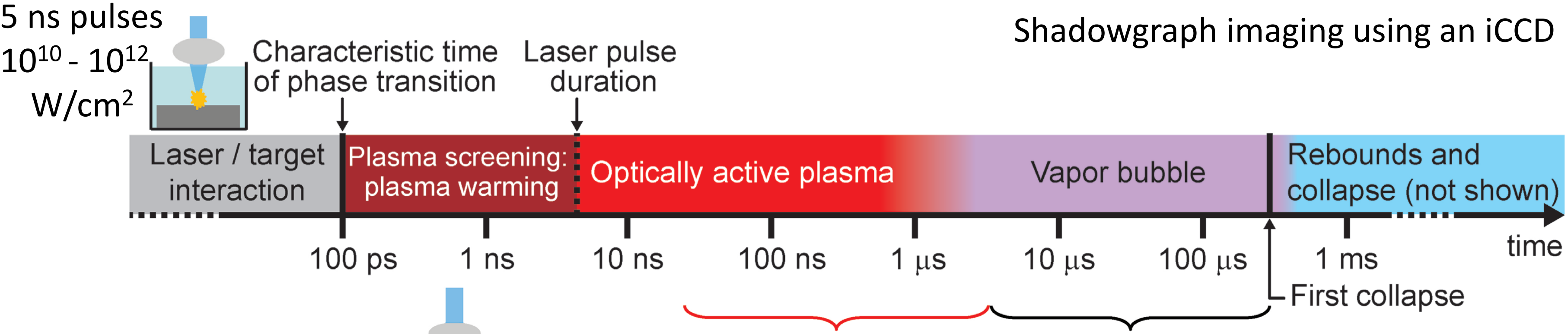




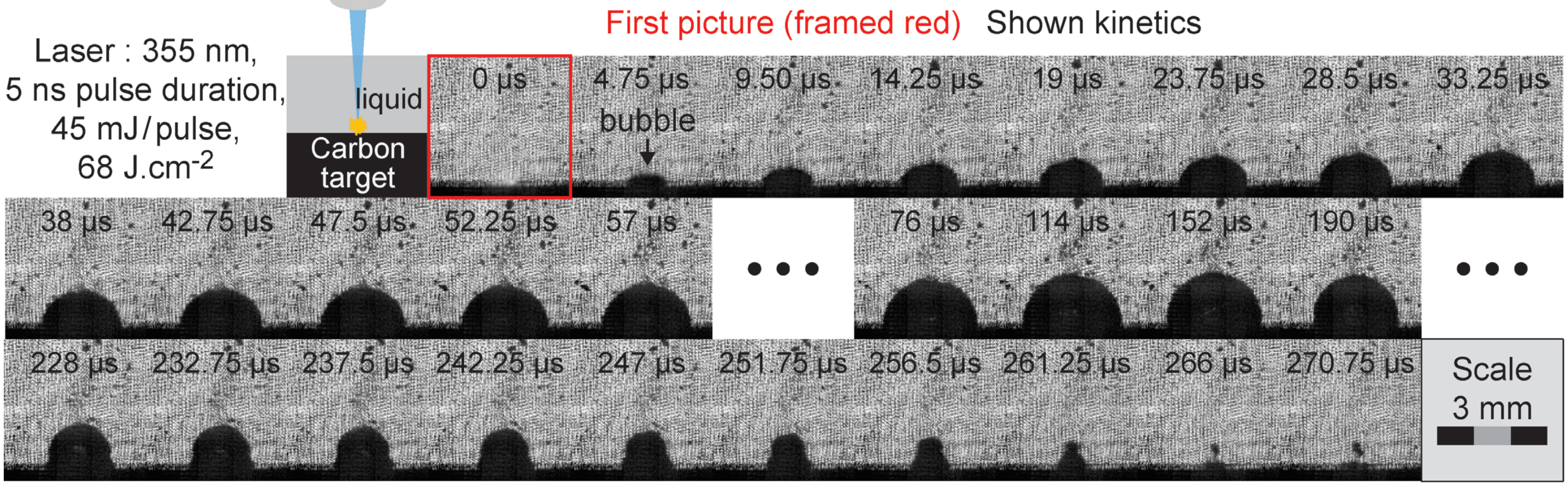
Characteristic time scales



Shadowgraph imaging using an iCCD



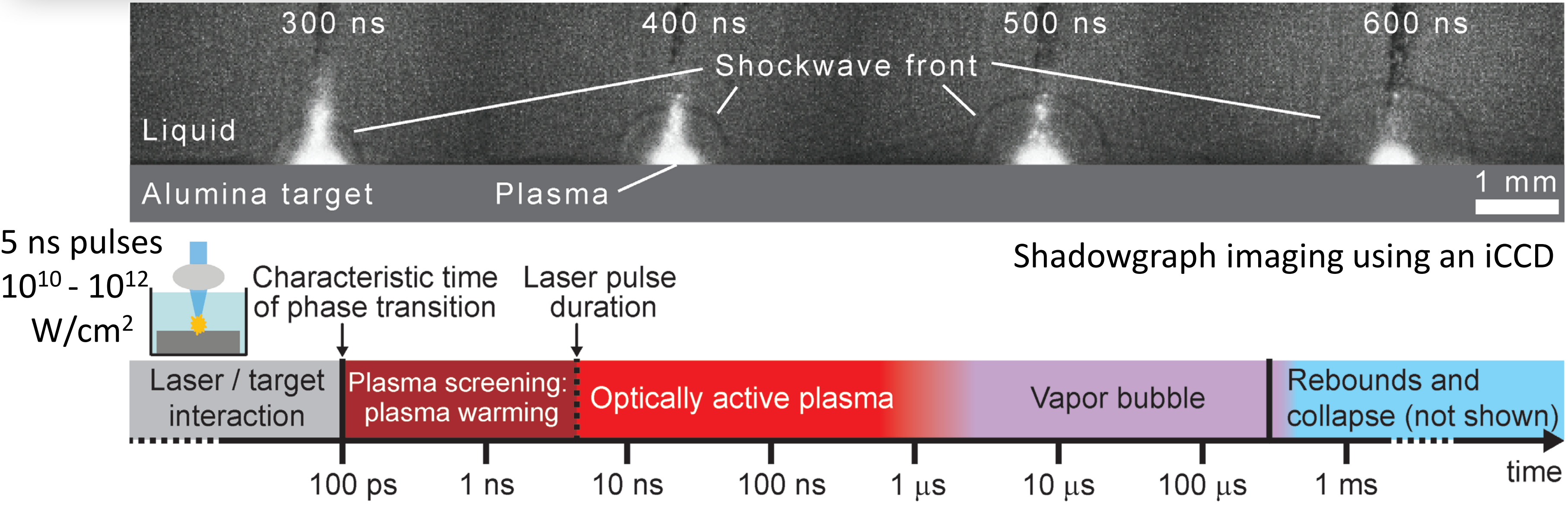
First picture (framed red) Shown kinetics



Shadograph imaging with fast camera

Amans *et al.*, J. Colloid. Interface Sci. **489**, 114-125 (2017).

Characteristic time scales

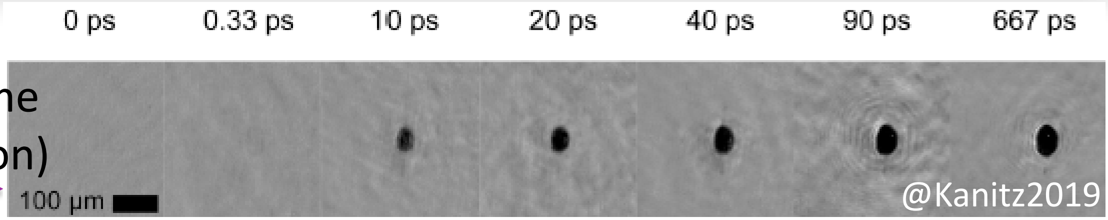


Shadowgraph imaging using an iCCD

<u>Original condition:</u>

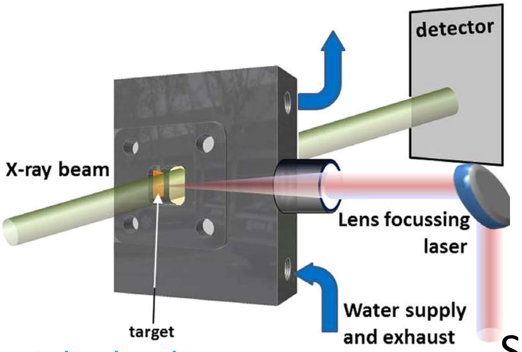
- **High pressure / Laser shock peening**
- **Fast cooling (a few µs vs. a few tens of µs in air)**
- **New category of plasma (T_e, N_e)**
- **Plasma-liquid interaction**

In-situ characterization



@Kanitz2019

Pump-probe microscopy [24-25] (charac. time e-/phonon, heat diffusion, phase transition)

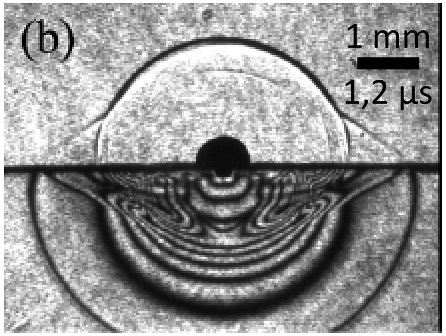


@Ibrahimkutty2015

Rayleigh-Mie scattering[12,13] (density, growth kinetics), Raman[19] (crystal structure)

small angle X-ray scattering [1,18] (particles diameter larger than few nm)

Shadowgraph[21,22] and Schlieren imaging[23] (shock waves)



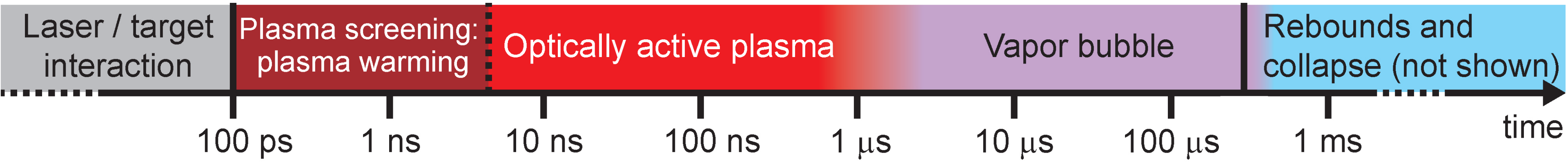
@Nguyen2013

acoustic signals[9-11] (shock waves release, cavitation lifetime)

Plasma Imagery [3-5,17] and shadowgraph fast imaging [2, 6-9,20] (P, V…)

Plasma spectroscopy[14-16] (species, T, electron density …)

Light induced fluorescence (species)



Laser / target interaction

Plasma screening: plasma warming

Optically active plasma

Vapor bubble

Rebounds and collapse (not shown)

In-situ characterization

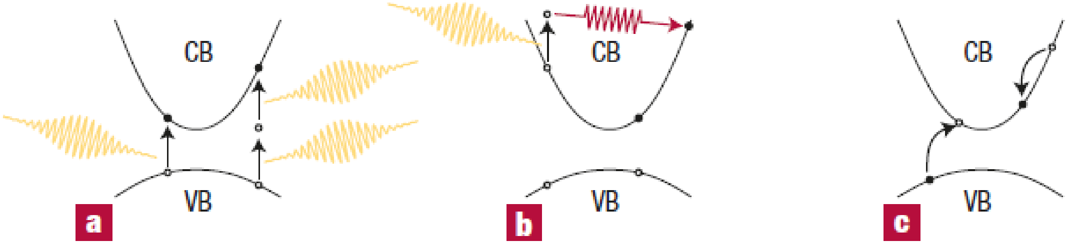
(1) S. Ibrahimkutty *et al.*, Appl. Phys. Lett. **101**, 103104 (2012) / S. Ibrahimkutty et al., Sci. Rep. **5**, 16313 (2015).
(2) T. Sakka *et al.*, Spectrochim. Acta, Part B **64**, 981 (2009).
(3) H. Oguchi *et al.*, J. Appl. Phys. **102**, 023306 (2007).
(4) K. Saito *et al.*, Appl. Surf. Sci. **197**, 56 (2002).
(5) B. Kumar *et al.*, J. Appl. Phys. **108**, 064906 (2010).
(6) K. Hirata *et al.*, Photon Proc. Microelec. Photonics IV, 2005, p. 311.
(7) T. Tsuji *et al.*, Jpn. J. Appl. Phys. **46**, 1533 (2007).
(8) K. Sasaki *et al.*, Pure Appl. Chem. **82**, 1317 (2010).
(9) T. Tsuji *et al.*, Appl. Surf. Sci. **254**, 5224 (2008).
(10) H. Jin *et al.*, Phys. Chem. Chem. Phys. **12**, 5199–5202 (2010).
(11) Zhu *et al.*, J. Appl. Phys. **89**, 2400 (2001)
(12) B. Kumar *et al.*, J. Appl. Phys. **110**, 074903 (2011).
(13) W. Soliman *et al.*, Appl. Phys. Express **3**, 035201 (2010).
(14) See bibliography of Tetsuo Sakka @ Kyoto University and Bhupesh Kumar @ Indian Institute of Technology Kanpur,
(15) J. Lam *et al.*, Phys.Chem.Chem.Phys. **16**, 963 (2014)
(16) A. Matsumoto *et al.*, J. Phys. Chem. C **119**, 26506 (2015).
(17) A. Tamura *et al.*, J. Appl. Phys. **117**, 173304 (2015).
(18) See bibliography of A. Pletch @ Karlsruhe Institute of Technology
(19) M. Takeuchi and K. Sasaki, Appl. Phys. A **122**, 312 (2016).
(20) J. Lam *et al.*, Appl. Phys. Lett. **108**, 074104 (2016)
(21) T.T.P. Nguyen et al., Appl. Phys. Lett. 102, 124103 (2013) / T.T.P. Nguyen et al., Optics and Laser Technology **100,** 21–26 (2018)
See bibliography of T. T. P. Nguyen @Nagaoka Univ. of Technology and then @Institute of Research and Development, Duy Tan Univ.
(22) Z. Zhang et al., AIP Advances 9, 125048 (2019)
(23) L. Martí-López et al., Appl. Opt. **48**, 3671 (2009)
(24) M. Domke et al., Appl. Phys A **109**, 409 (2012) / See bibliography of Heinz P. Huber @ Munich University of Applied Sciences
(25) A. Kanitz et al., Appl. Surf. Sci. **475,** 204 (2019).

Non-exhaustive list !

Ask me !

Contents

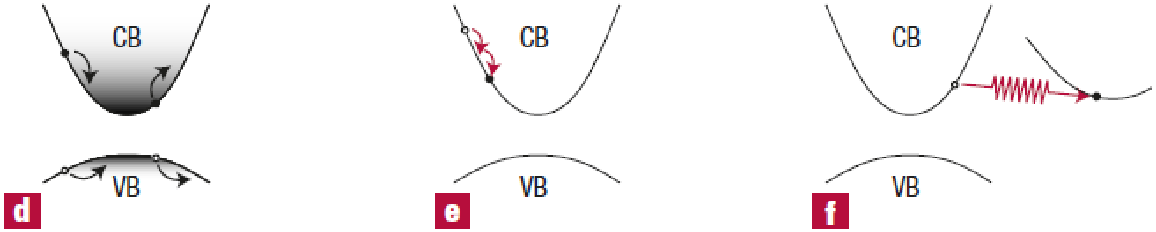
CARRIER EXCITATION



a Multiphoton absorption.
b Free-carrier absorption.
c Impact ionization.

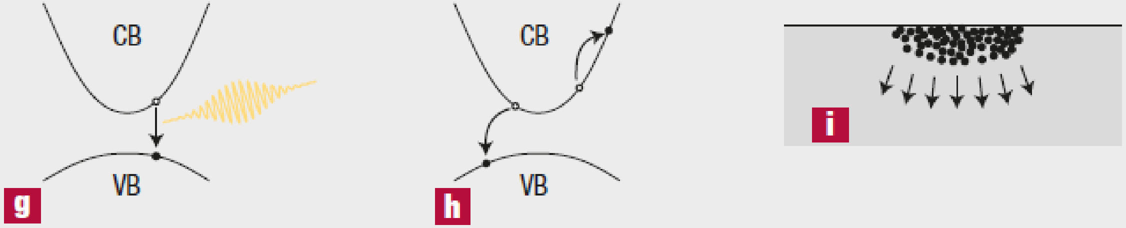
THERMALIZATION

d Carrier distribution before scattering.



e Carrier–carrier scattering.
f Carrier–phonon scattering.

CARRIER REMOVAL



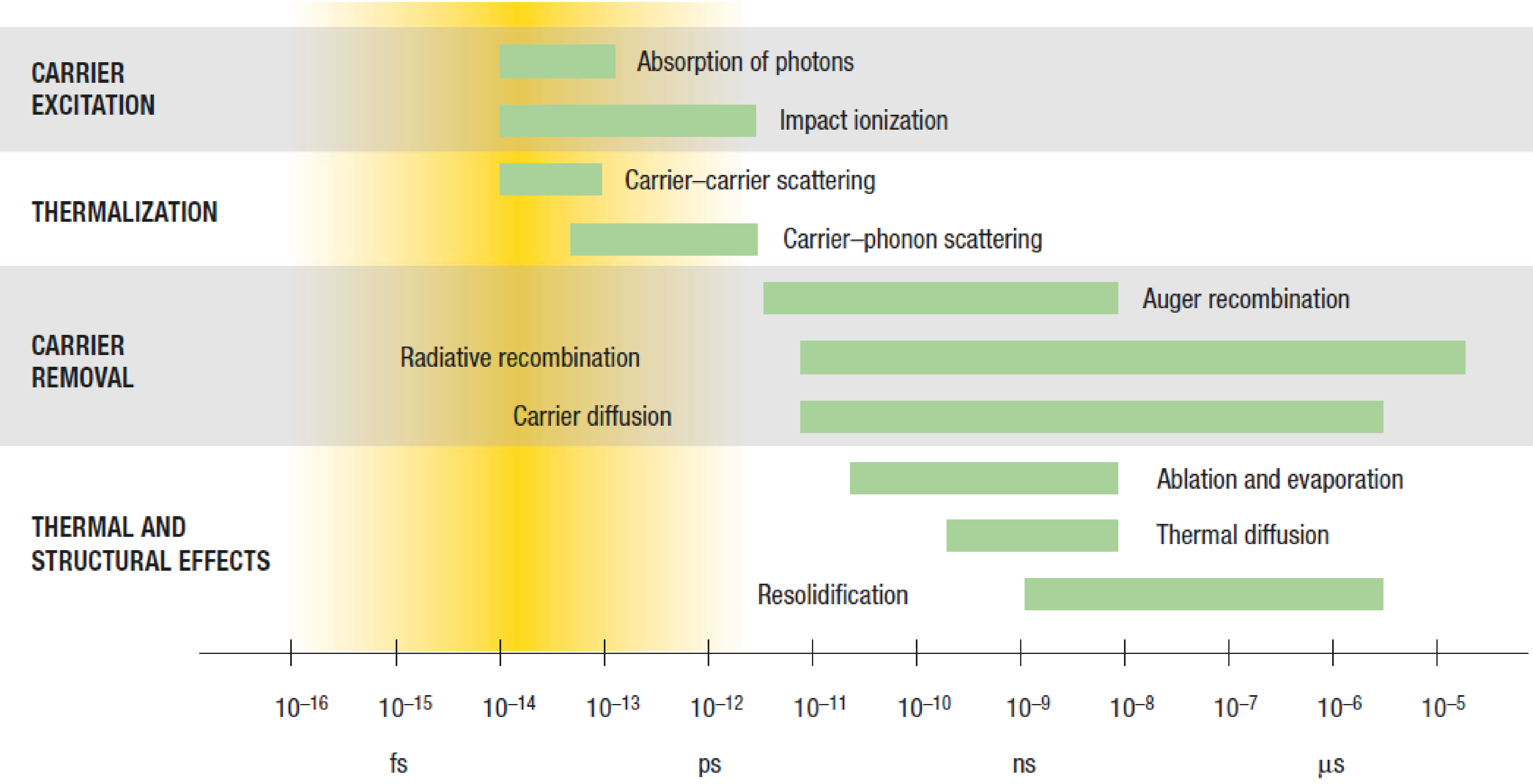
g Radiative reomb.
h Auger recomb.
i Diffusion of excited carriers

THERMAL AND STRUCTURAL EFFECTS

j Thermal diffusion
k Ablation…

S. K. Sundaram et al., nature materials 1, 217 (2002)

Characteristic time scales in laser ablation

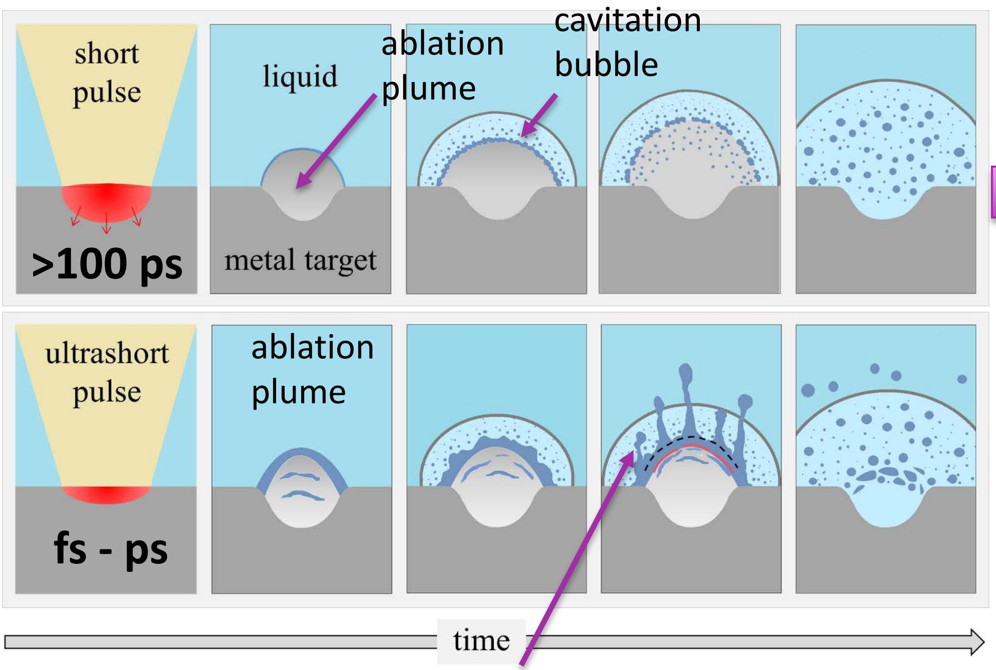


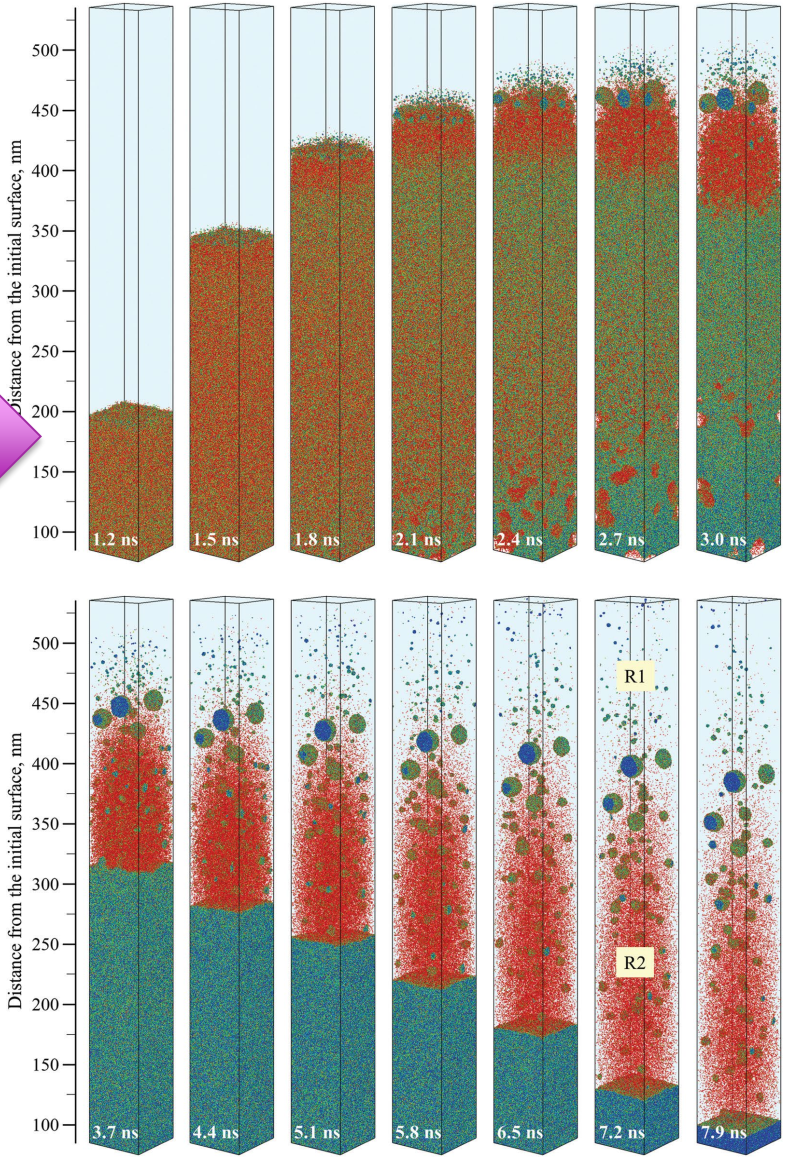
S. K. Sundaram et al., nature materials 1, 217 (2002)

Characteristic time scales in laser ablation

Ag target, 400ps, 600 mJ/cm^2, 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

See bibliography of C.-Y. Shih & L. V. Zhigilei @ University of Virginia

Shock waves

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

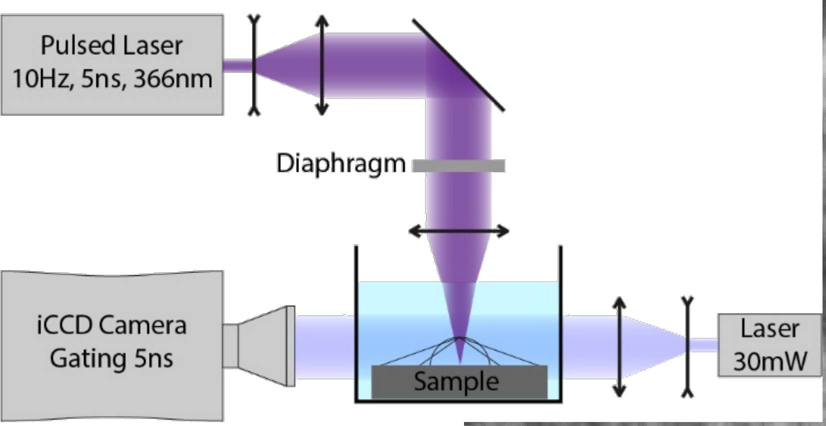
Shock waves

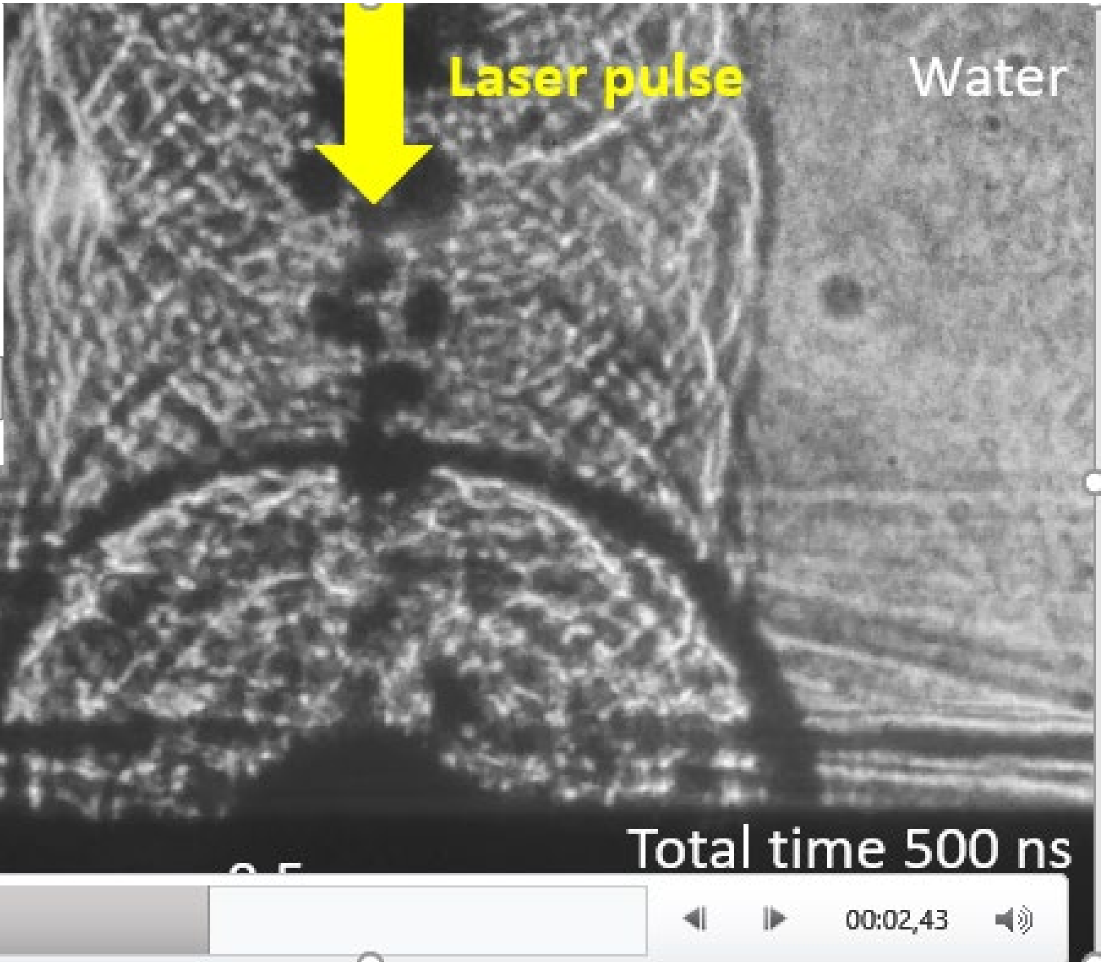
Laser pulse (5ns, > 10^{10} W/cm^2)

Phase transition

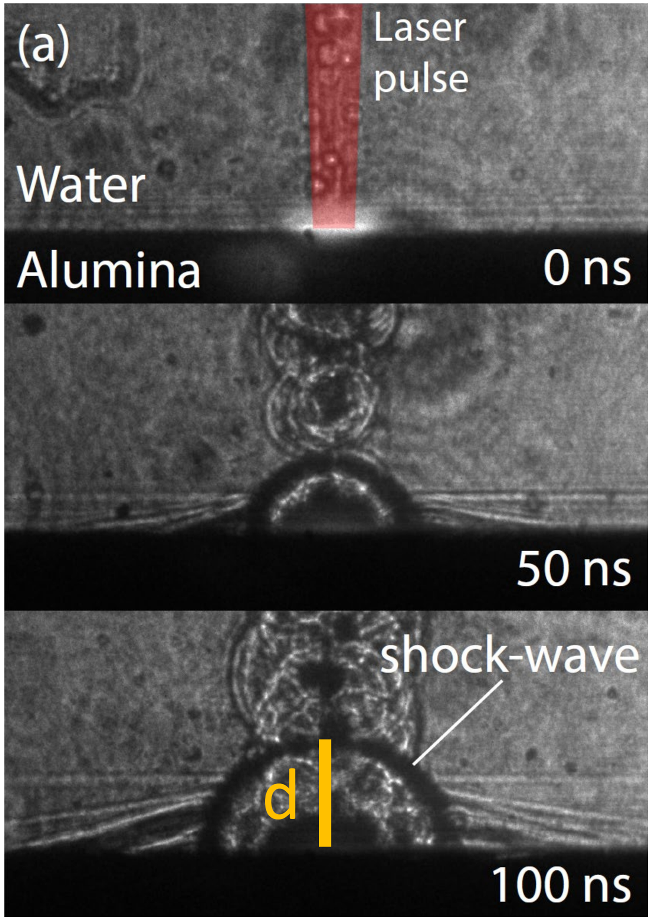
Large Pressure (GPa)

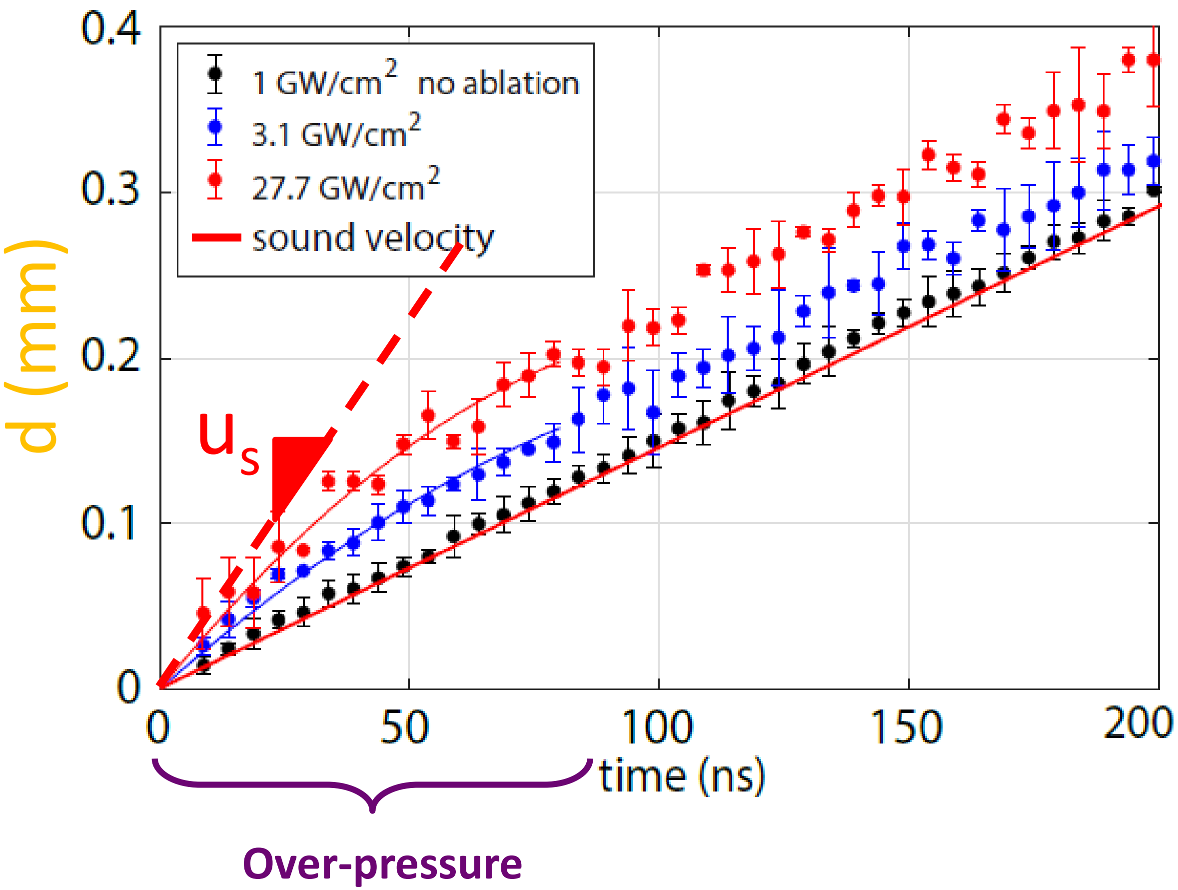
Shock-waves





Shock front kinematics





Shock waves

Conservation of momentum at a shock front:

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

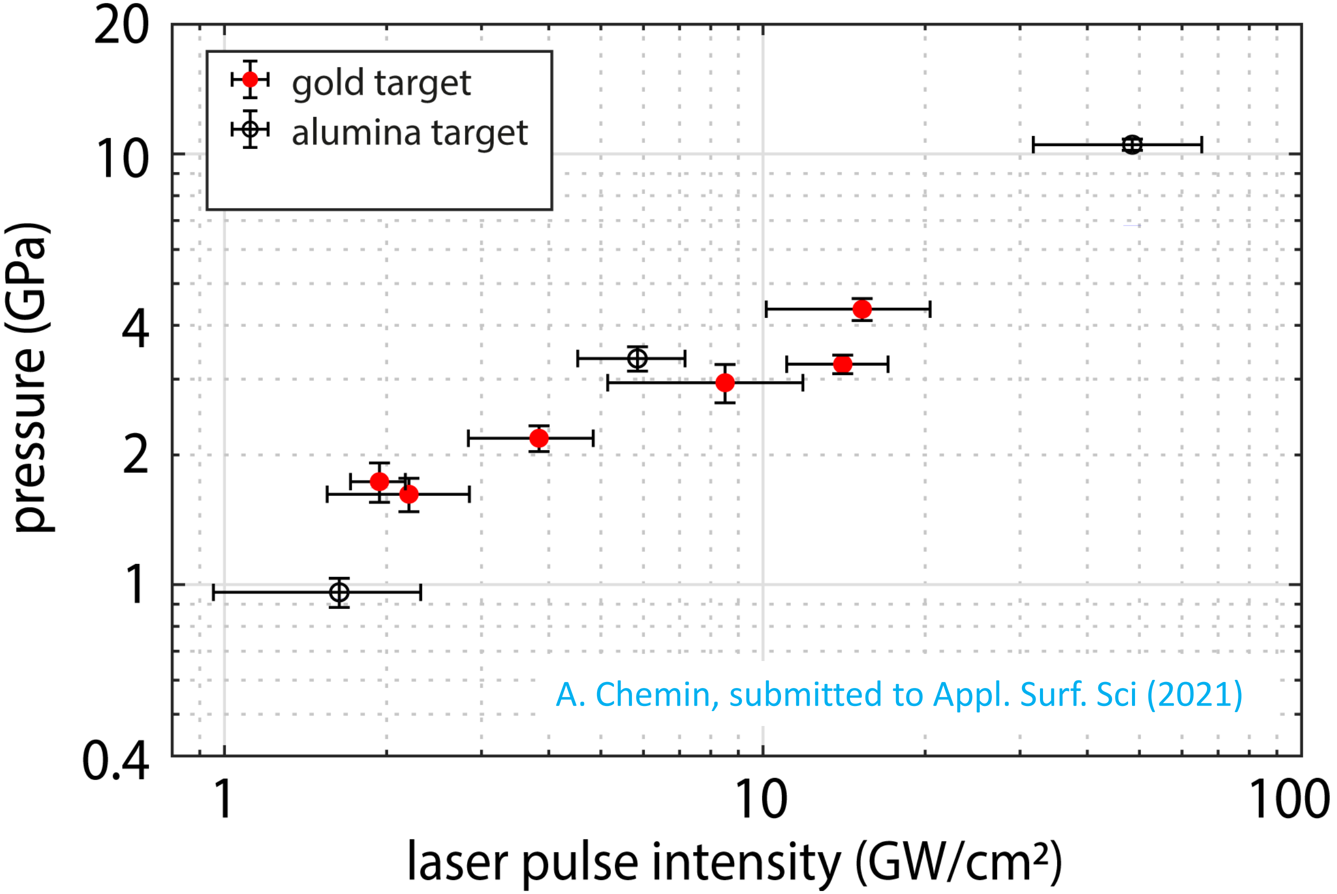
u_p : particles velocity

Hugoniot curve from Rice and Walsh:

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

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

Valid up to 25 GPa



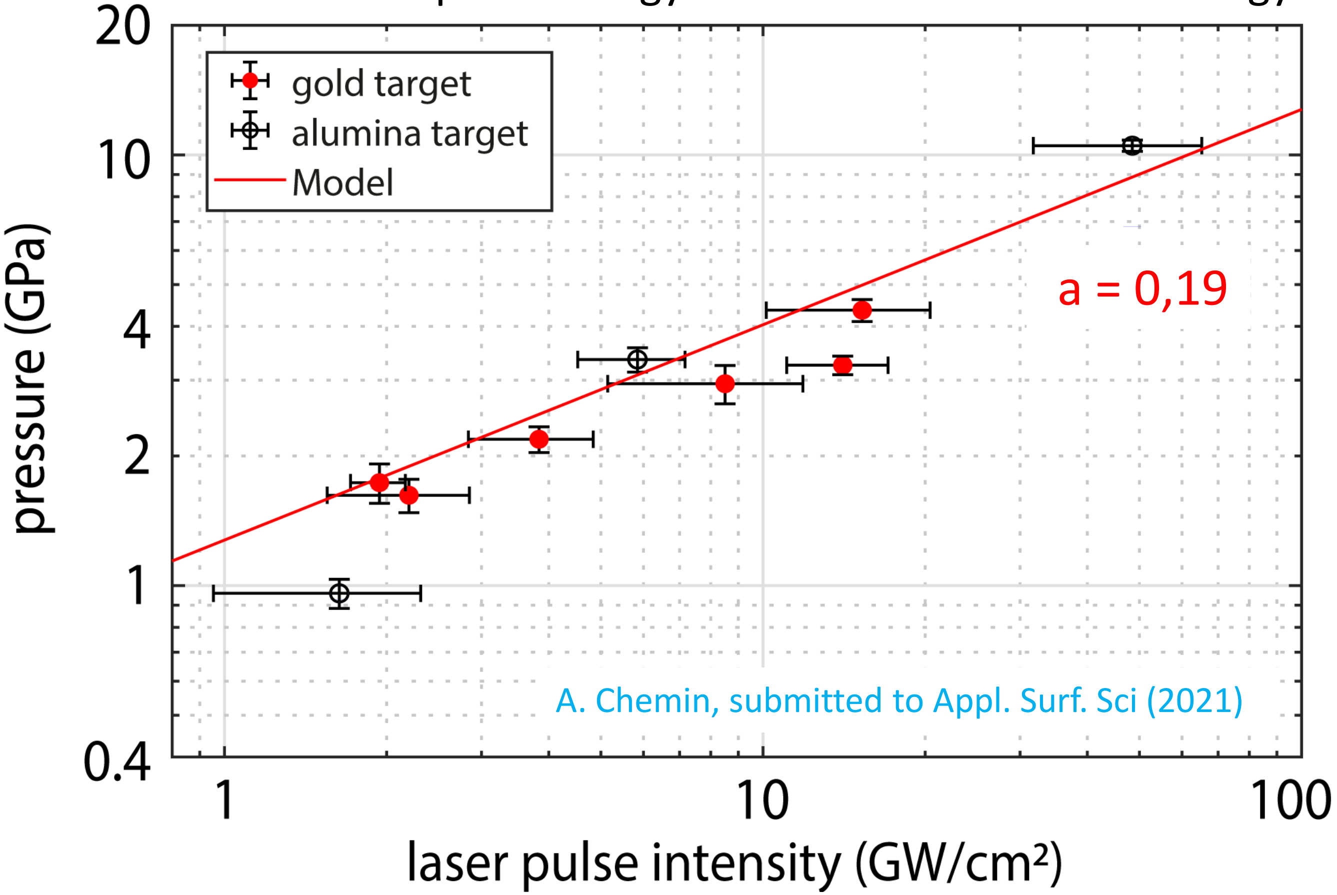
A. Chemin, submitted to Appl. Surf. Sci (2021)

Shock waves

Relates the initial pressure to the pulse energy : $p_s(MPa) = 10\sqrt{\frac{a}{2a+3}ZI}$

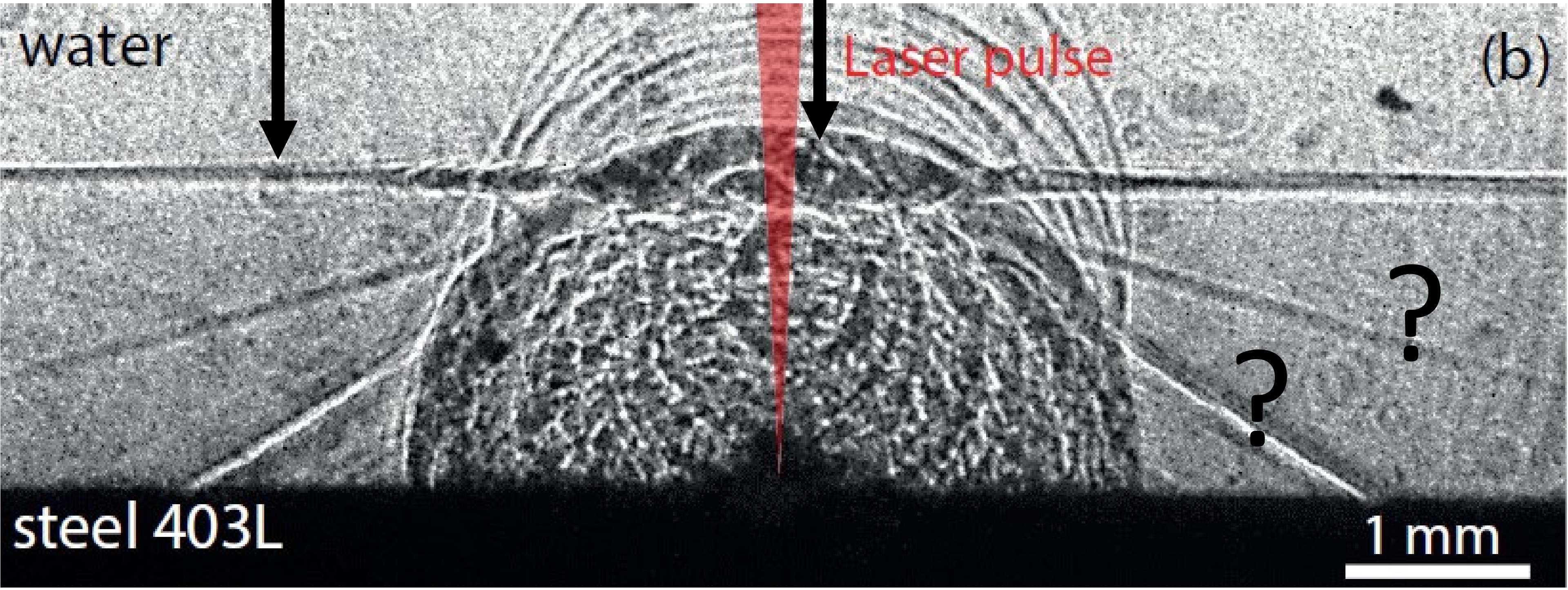
R. Fabbro et al. J. Appl. Phys. **68**, 775 (1990)

Z the reduced acoustic impedence
I the laser intensity [W/cm^2]
a fraction of pulse energy involved in the thermal energy



A. Chemin, submitted to Appl. Surf. Sci (2021)

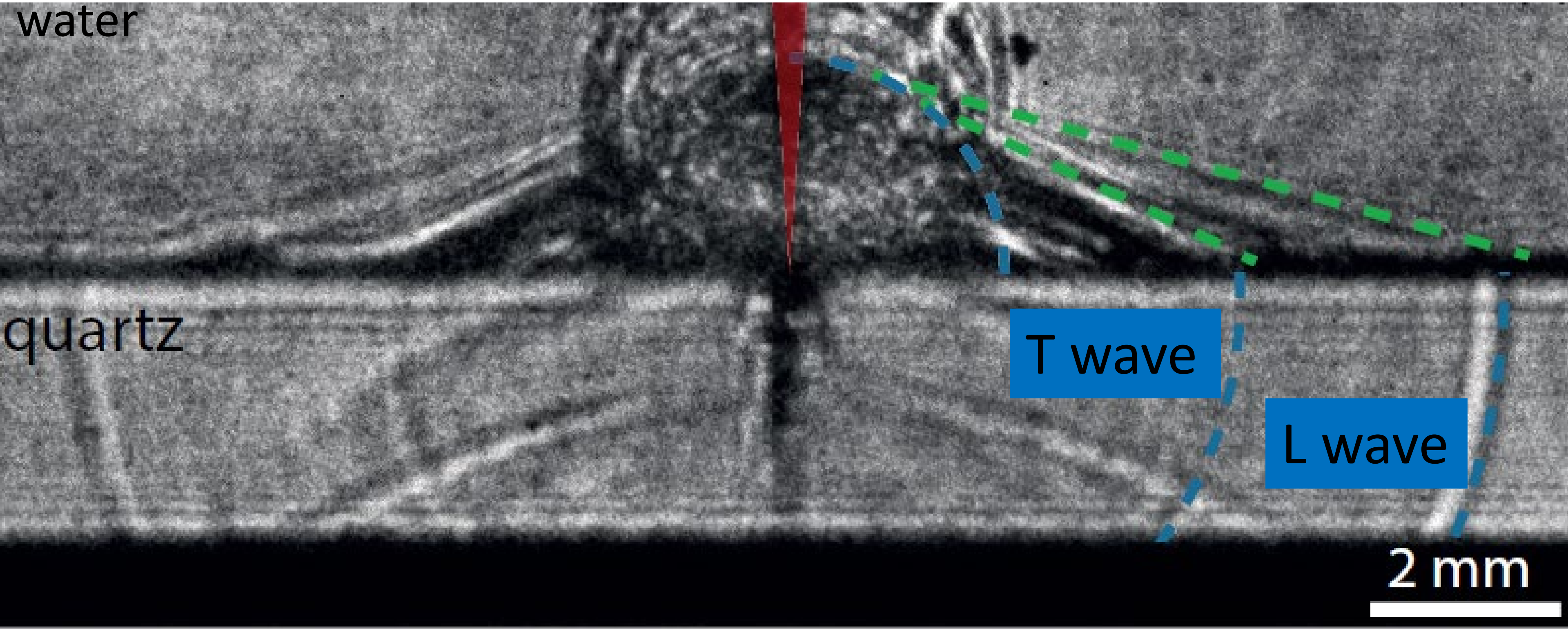
Origin the observed shock waves ?



Due to scattered light heating the target's surface

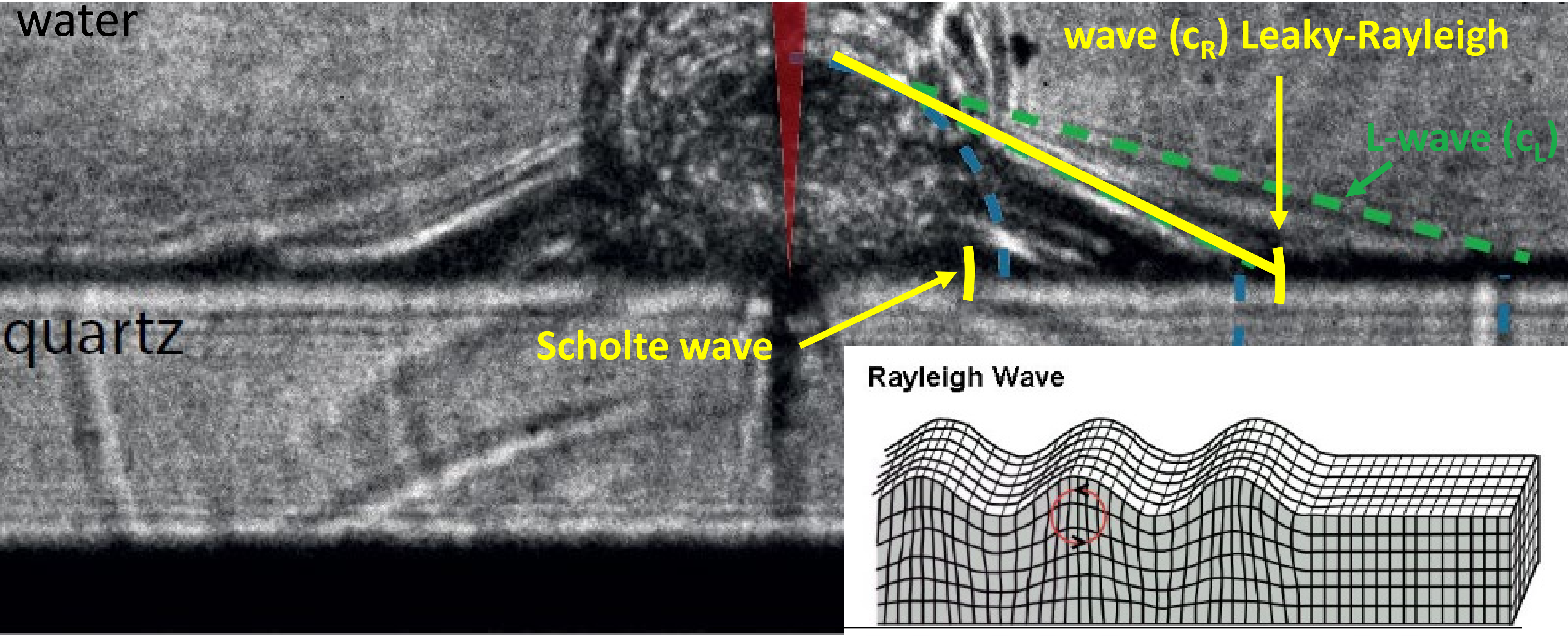
Direct Blast

Shock waves in the target & couplings



→ Due to Shock-waves in the target ?

Shock waves in the target & couplings



→ Due to Shock-waves in the target ? Yes for the L-wave

→ **Surface waves** at the interface between the liquid and the target: Scholte-wave (not observed) and the leaky-Rayleigh wave

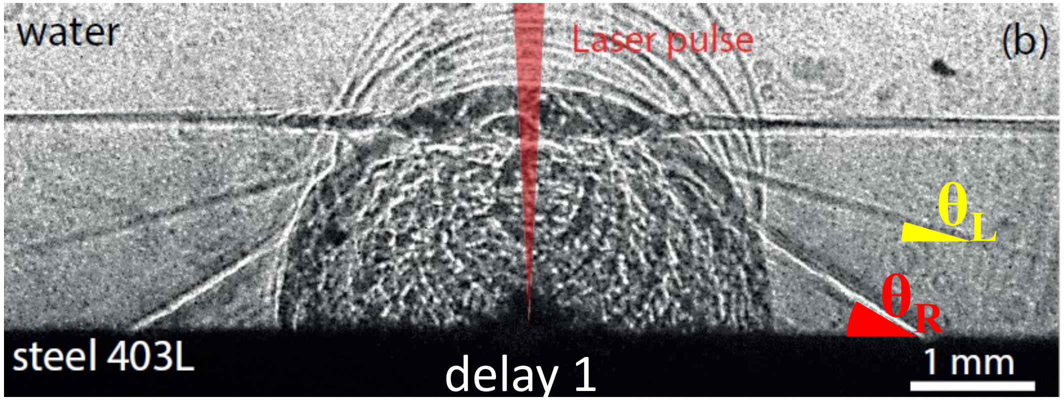
Measurement of elastic modulus (E, ν)

Measurement

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

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

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:

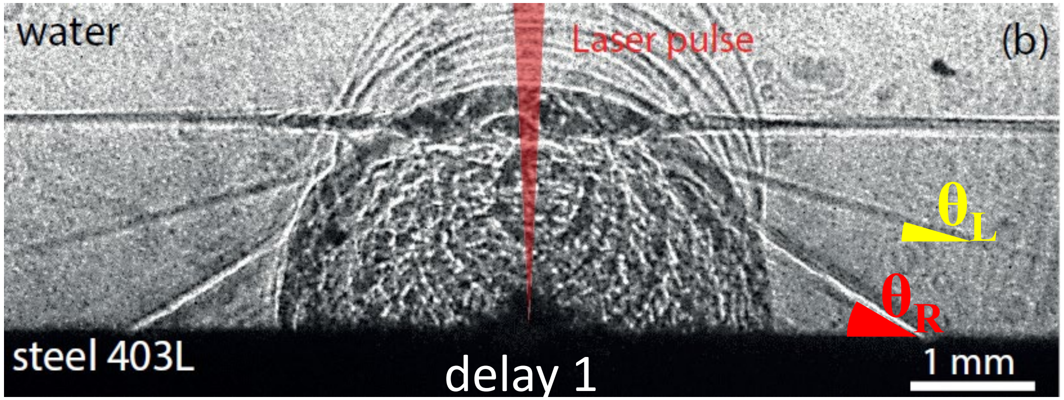
$$c_T = \sqrt{\frac{1}{2(1+\nu)}\frac{E}{\rho}} \qquad c_L = \sqrt{\frac{1-\nu}{(1+\nu)(1-2\nu)}\frac{E}{\rho}}$$

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

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

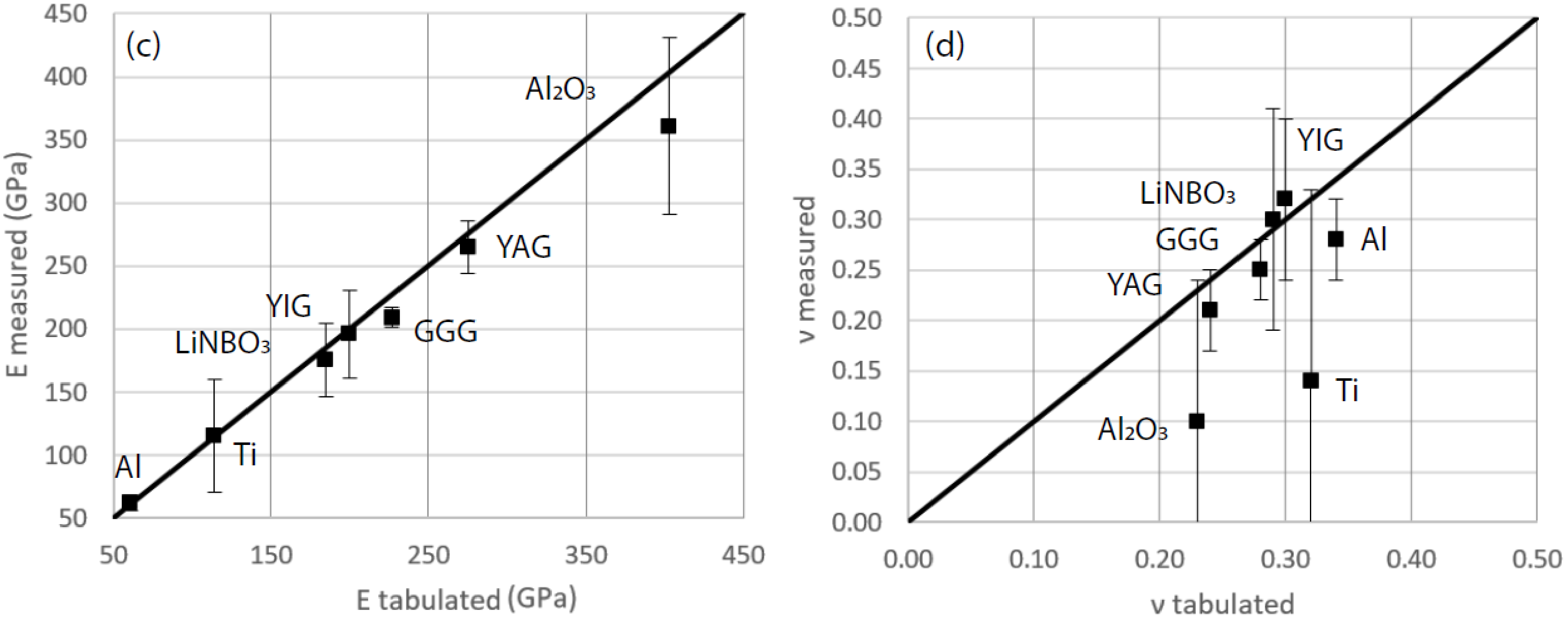
Determination of E/ρ

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

Depends only on the angles!

A. chemin, M. Fawaz, T. Vidril et D. Amans : « Procédé de mesure d’un module d’élasticité par génération laser d’ondes de surface à une interface matériau/liquide », demande de brevet français n° 2105079 déposée le 14 mai 2021.

Measurement of elastic modulus (E, ν)

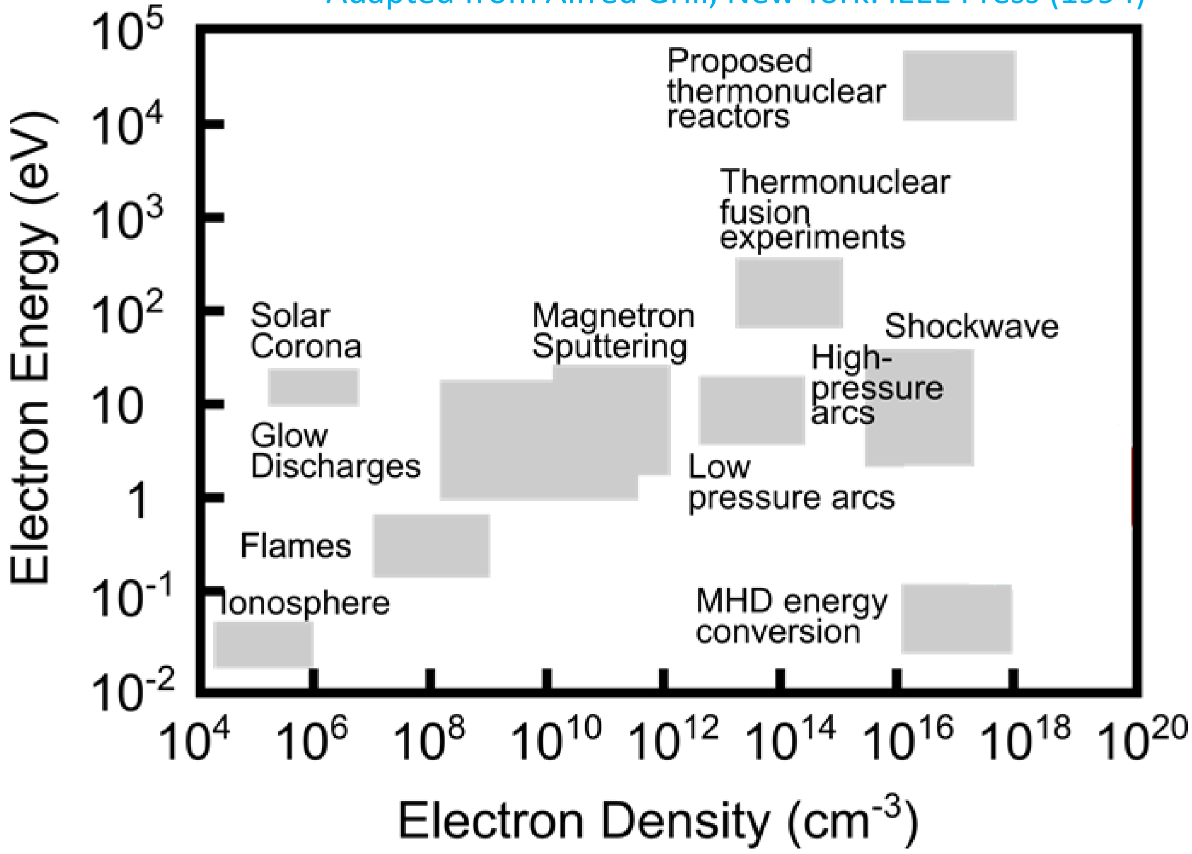


Comment : using an exact method provides same results given the measurement errors.

Plasma spectroscopy

- ➢ **Plasma classification**
- ➢ **Density**
- ➢ **Temperatures**
- ➢ **LIBS underwater ?**

Classification of plasmas



Adapted from Alfred Grill, New York: IEEE Press (1994)

?

We can expect:
High density
Low temperatures

Necessary condition regarding the local Thermodynamic Equilibrium for the electronic states

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

H. Drawin, Zeitschrift fur Physik, 1969, 228, 99.

Plasma spectroscopy

Plasma spectroscopy : measurement of thermodynamic parameters

- **Plasma species and time evolution of the chemical composition**

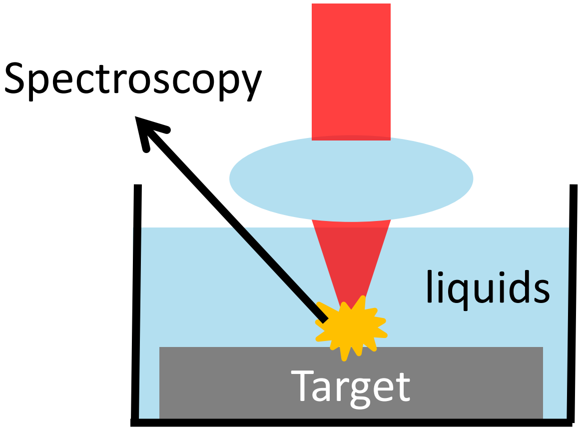
  atomic / ionic / molecular lines indexation

- **Plasma temperatures**

  diatomic molecules : $T_{rotational}$, $T_{vibrational}$
  Electronic temperature of atoms, ions molecules : T_{elec}
  (electrons (kinetics) : T_e)

- **Electron density (n_e):**

  Electronic field => Stark effects (broadening and shift)



Plasma spectroscopy: Ro-vibrational spectroscopy

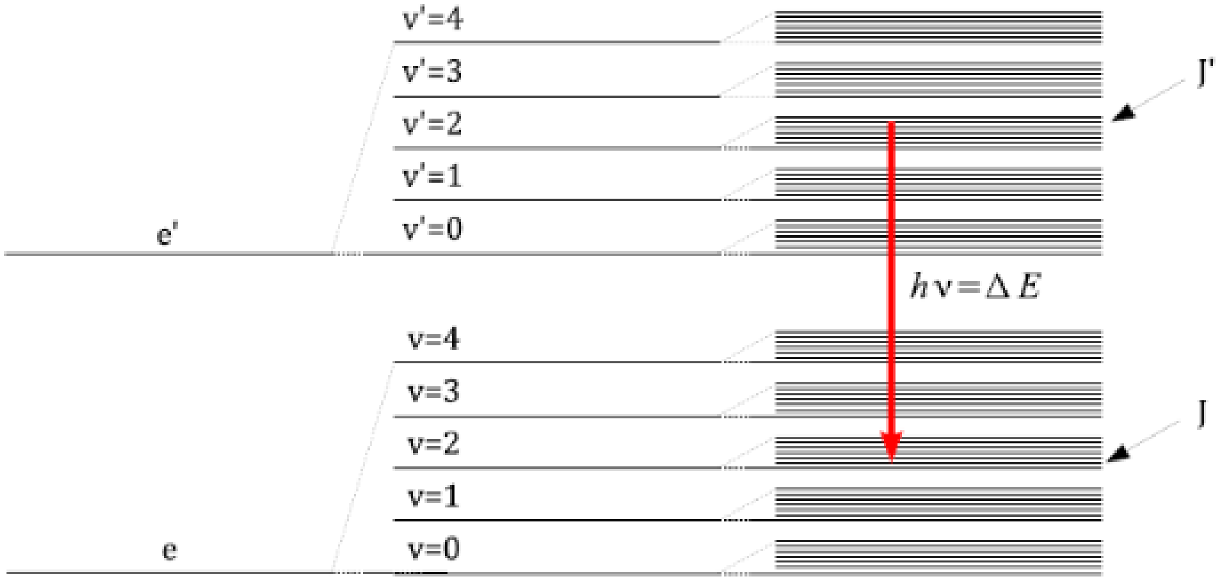
canonical ensemble

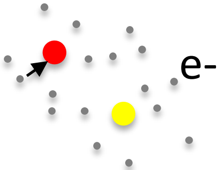
Temperatures:

- Atoms : $E = T_n$ → T_{elec}
- Diatomic molecules : $E = T_n + G_n(v) + F_v(J)$ → T_{elec} , T_{vib} , T_{rot}

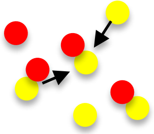
T_{elec} T_{vib} T_{rot}

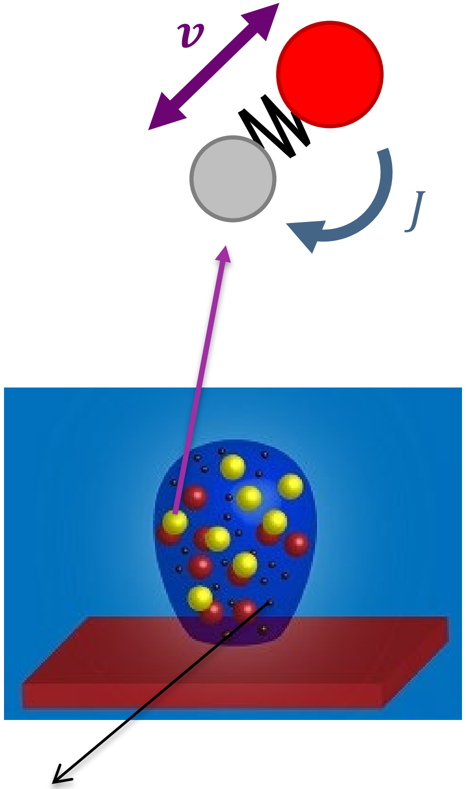
Electronic levels | Vibrational levels | Rotational levels





$\neq$





Electron : Kinetic temperature T_e

Plasma spectroscopy: Ro-vibrational spectroscopy

$$E = T_n + G_n(v) + F_v(J)$$

… but $F_v(J)$ Depend on the Hund's case ($\vec{S}$, $\vec{L}$, $\vec{N}$ and their projection)

Istvan Kovacs (1969)

$$\left.\begin{aligned} G_n(v) &= w_e\left(v+\frac{1}{2}\right) - w_e x_e\left(v+\frac{1}{2}\right)^2 + w_e y_e\left(v+\frac{1}{2}\right)^3 + \dots \quad (cm^{-1}). \\ F_v(J) &= B_v \cdot J(J+1) - D_v \cdot \Big(J(J+1)\Big)^2 + \dots + H(J,K,S,\Lambda,\Sigma\dots) \quad (cm^{-1}) \end{aligned}\right\}$$

Tabulated

$$I^{n',v',J'}_{n'',v'',J''} = hc \cdot \cancel{\bar{\nu}^{n',v',J'}_{n'',v'',J''}} \cdot A^{n',v',J'}_{n'',v'',J''} \cdot N_{n',v',J'} \qquad (W \cdot m^{-3}).$$

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 $A^{n',v'}_{n'',v''} = \frac{1}{4\pi\varepsilon_0}\frac{64\pi^4}{3h(2-\delta_{0,\Lambda'})(2S'+1)} \cdot (100 \cdot \bar{\nu}^{n',v',J'}_{n'',v'',J''})^3 \cdot S^{n',v'}_{n'',v''} \cdot (a_0 e)^2$

$$A^{J'}_{J''} = \frac{S^{J'}_{J''}}{2J'+1}$$

Höln-London's coefficient

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

Normalisation, Istvan Kovacs (1969)

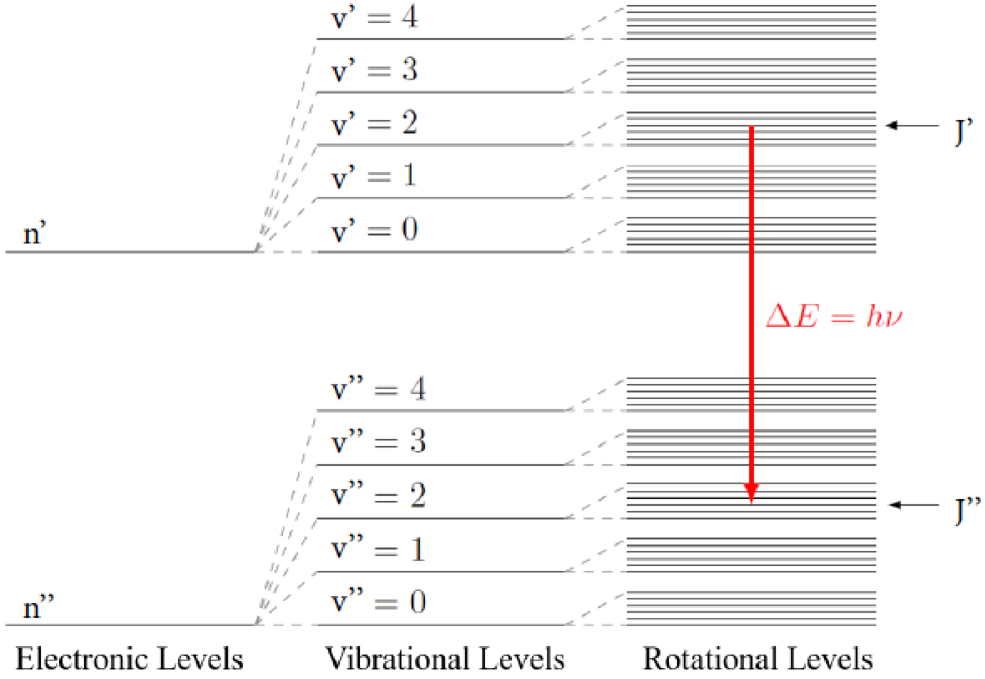
$$N_{n',v',J'} = N_{n'} \cdot \frac{1}{2} \cdot (2J'+1) \cdot \frac{exp\left(-\frac{hc \cdot F_{v'}(J')}{k_B \cdot T_{rot}}\right)}{Q_{rot_{n',v'}}(T_{rot})} \cdot \frac{exp\left(-\frac{hc \cdot G_{n'}(v')}{k_B \cdot T_{vib}}\right)}{Q_{vib_{n'}}(T_{vib})}$$

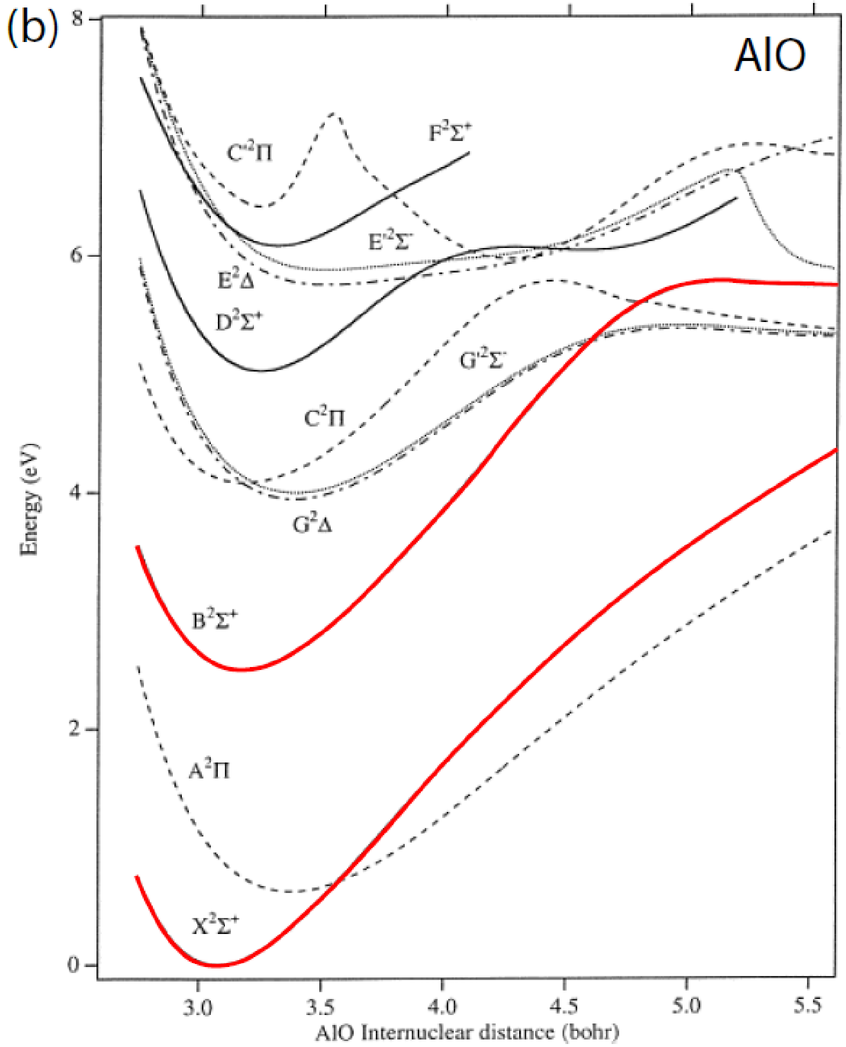
Population density of the **excited state**

Plasma spectroscopy: Ro-vibrational spectroscopy

$AlO(B^2\Sigma^+) \longrightarrow AlO(X^2\Sigma^+)$

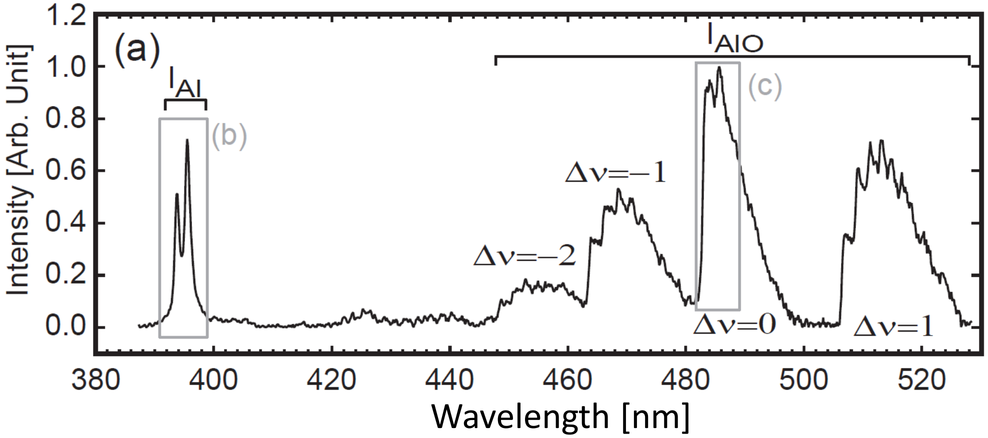
visible light (~ 500 nm)

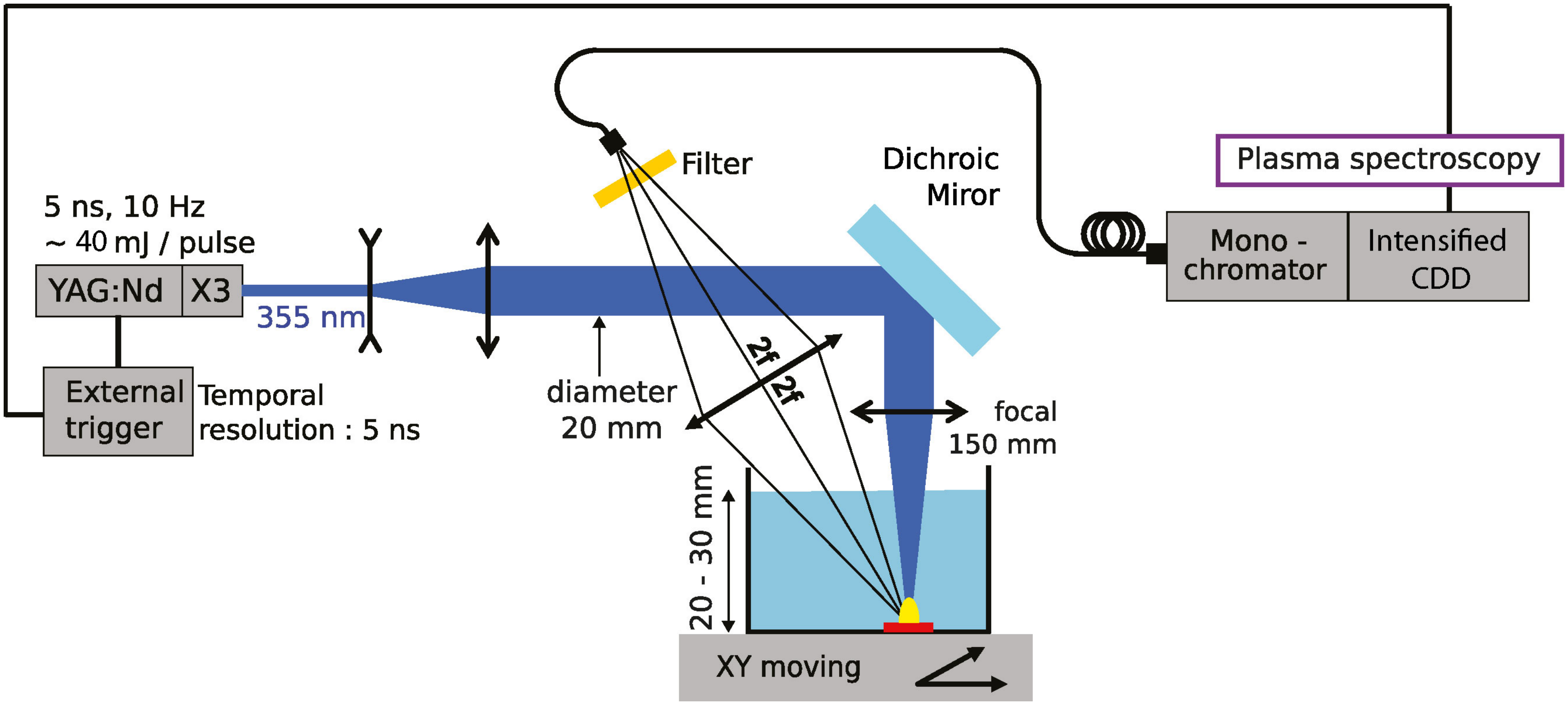




Plasma spectroscopy

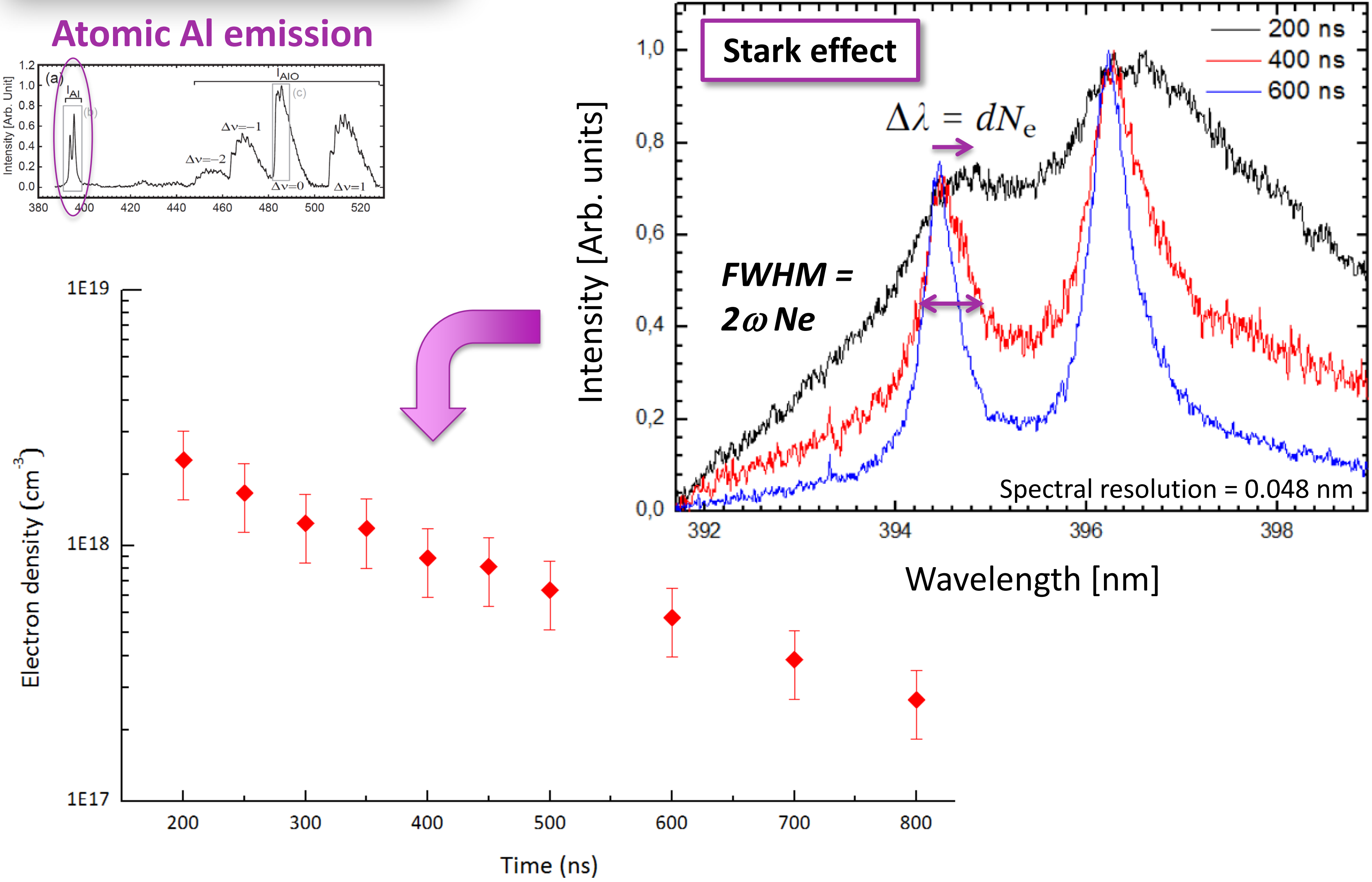
Exemple on Al_2O_3 target





Plasma spectroscopy: Electron density

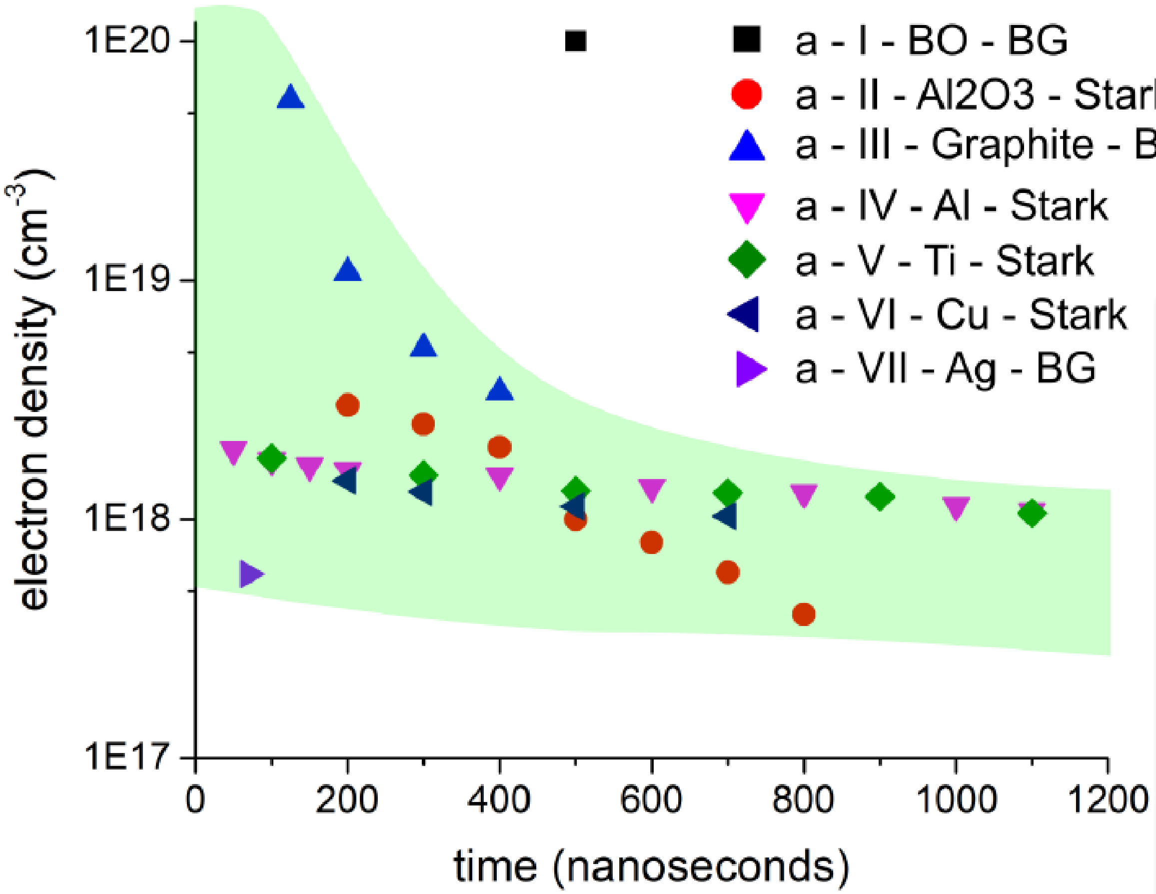
Atomic Al emission



J. Lam et al., Phys.Chem.Chem.Phys. **16**, 963 (2014)

Plasma spectroscopy: Electron density

BG : Background emission
Stark : Stark shift/broadening



[Review] A. Kanitz et al., Plasma Sources Sci. Technol. (2019)

If continuous emission is dominated by radiative electron-ion recombination.

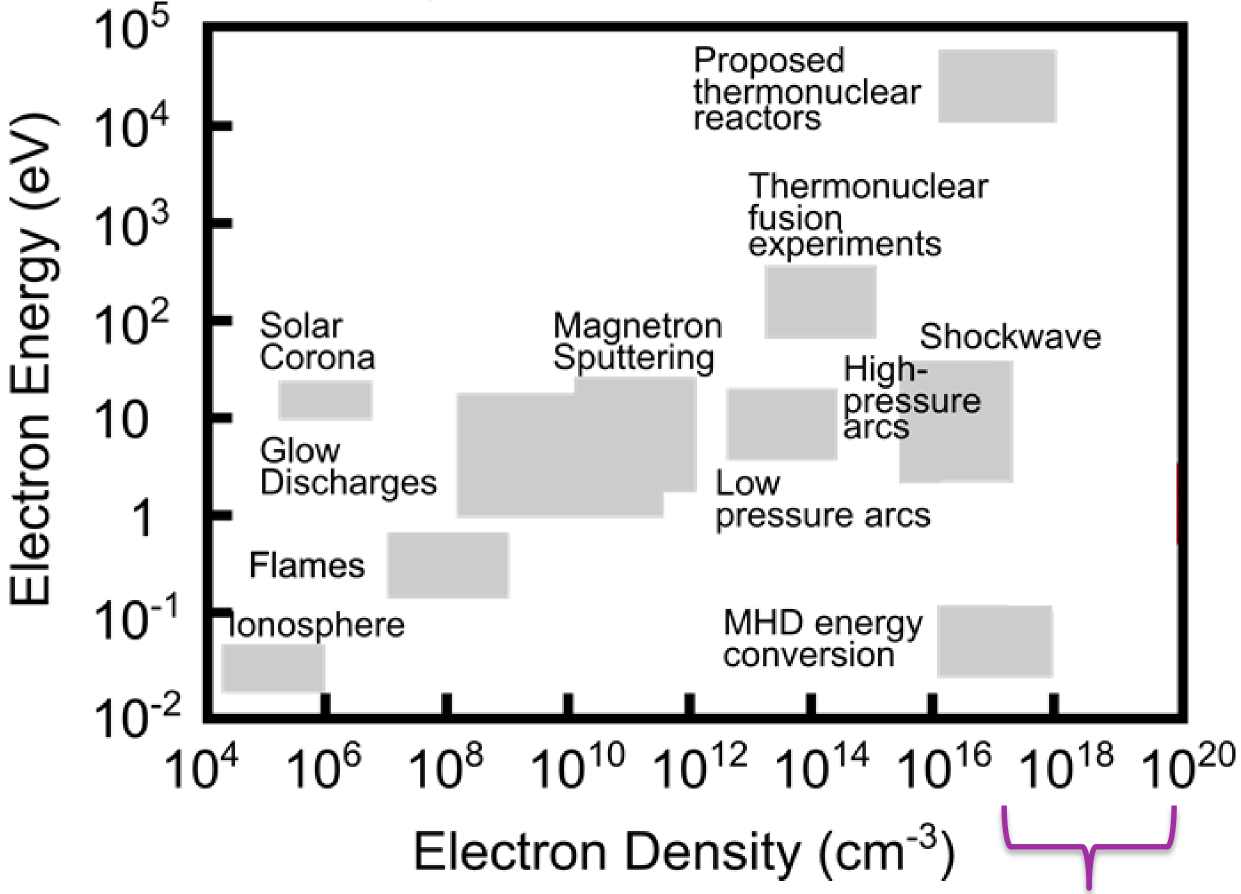
T. Sakka et al., J. Chem. Phys. 112, 8645 (2000)

$$n_e(t) = \frac{n_e(t_0)}{1 + \ (t - t_0)/\tau}$$

$$\tau = \left(\underset{\substack{\uparrow \\ 10^{-12}\,\mathrm{cm^3.s^{-1}}}}{\alpha}\, n_e(t_0)\right)^{-1}$$: decay time back. emi.

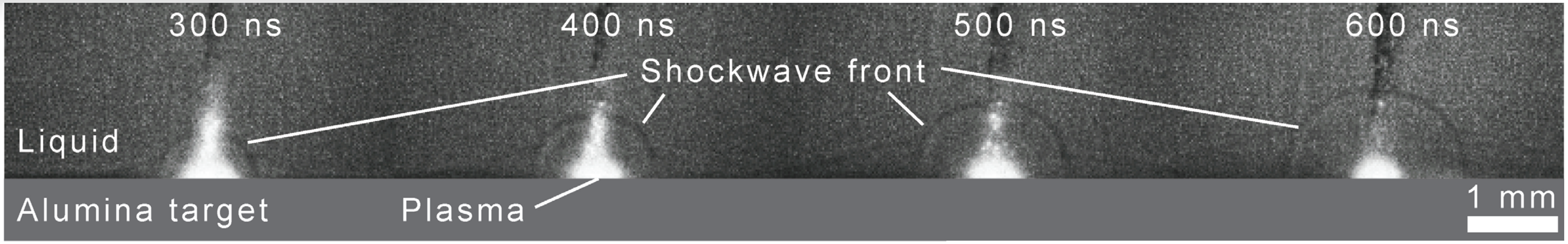
Classification of plasmas

Adapted from Alfred Grill, New York: IEEE Press (1994)

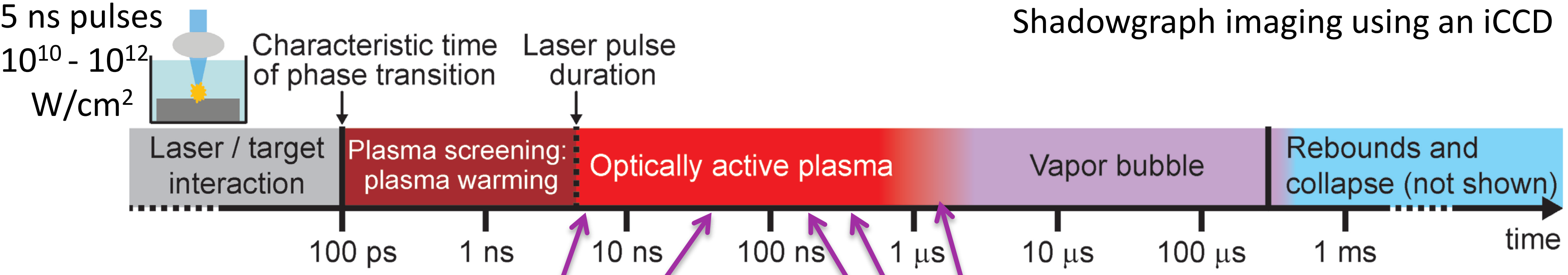


Here… good news for what concerns the local thermodynamic equilibrium for the electronic states

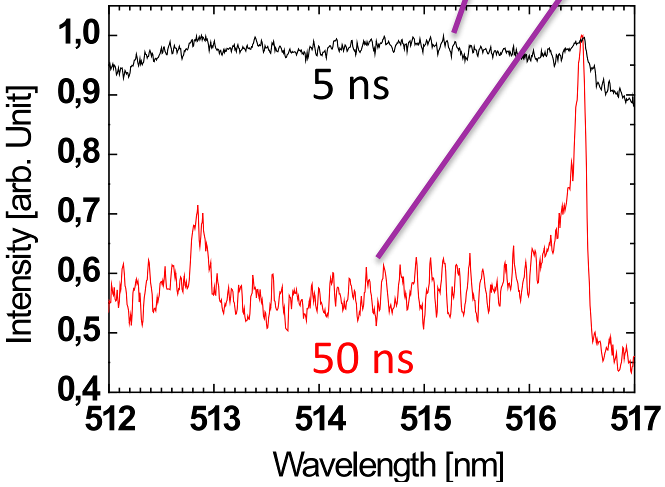
Plasma spectroscopy



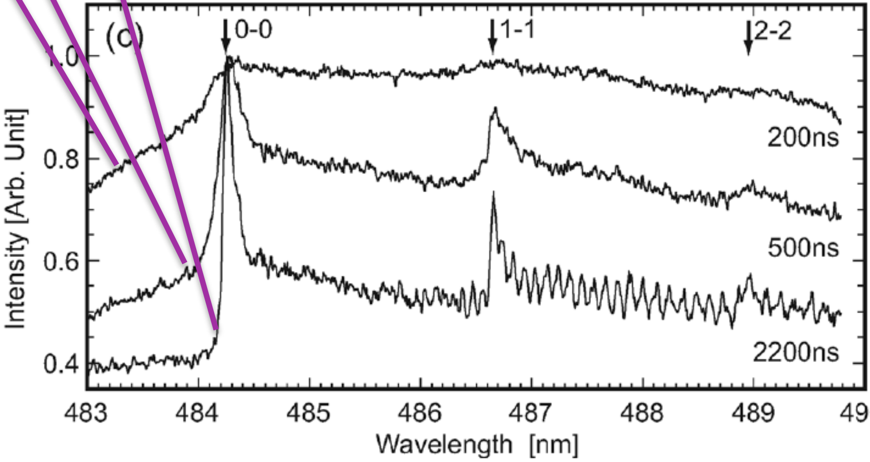
Shadowgraph imaging using an iCCD



Carbon target -> C_2 swan band



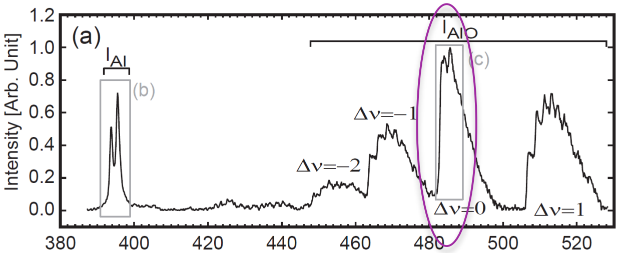
Al_2O_3 target -> AlO molecules



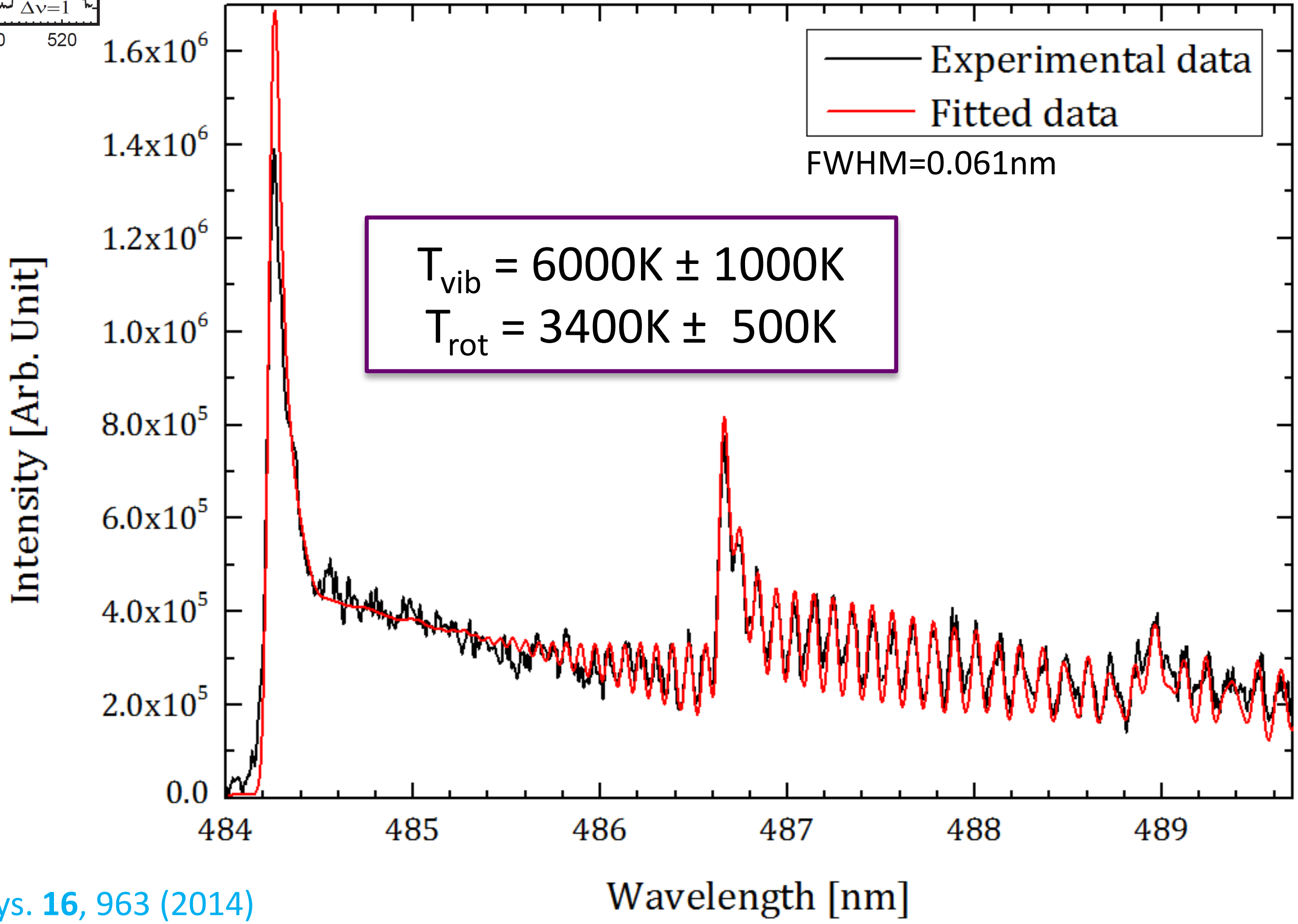
Molecules appear early (with respect to what is observed in gas or vacuum) -> problem for LIBS

Plasma spectroscopy: Temperatures

Atomic AlO emission



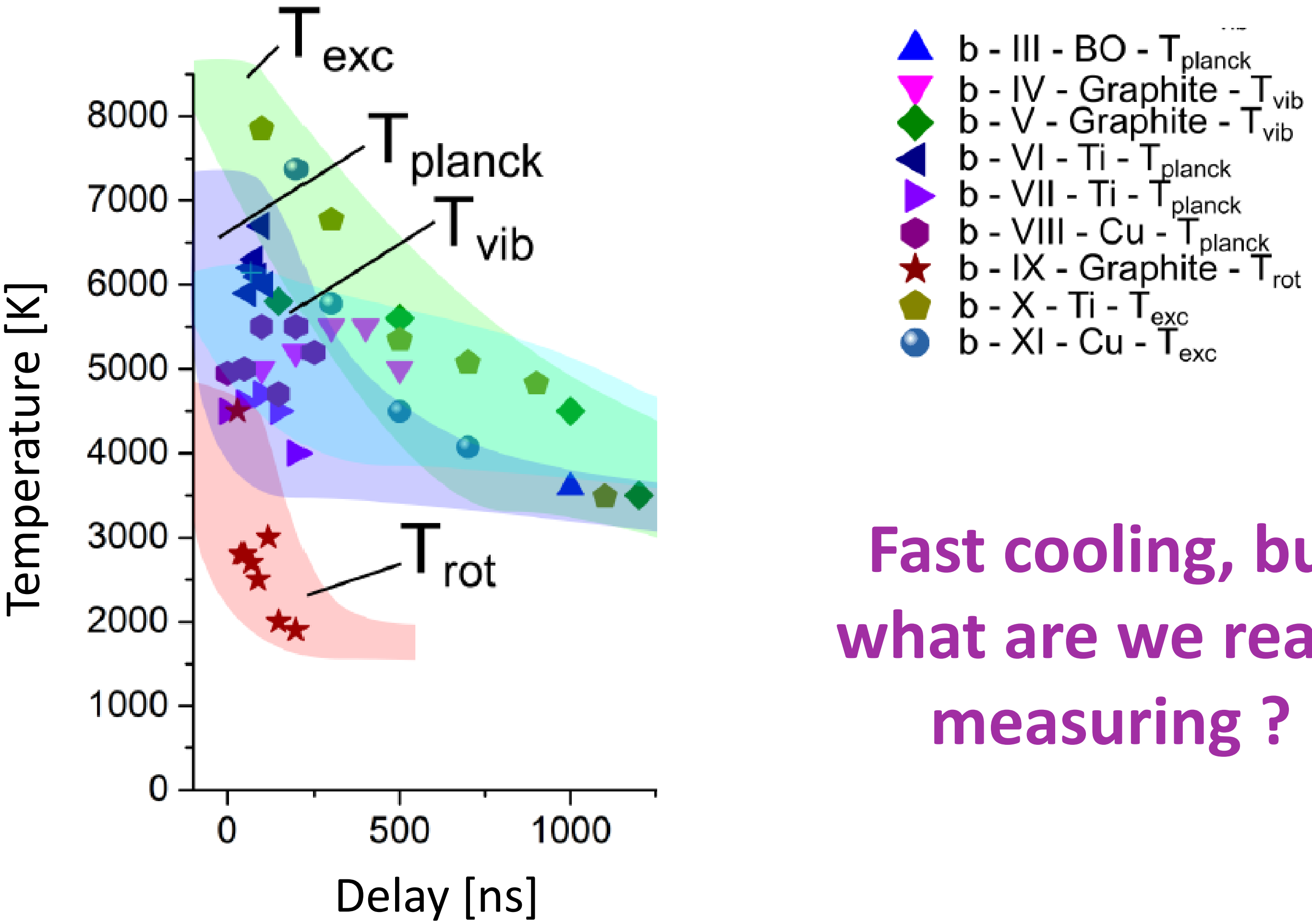
AlO molecules emission



T_{vib} = 6000K ± 1000K
T_{rot} = 3400K ± 500K

J. Lam et al., Phys.Chem.Chem.Phys. **16**, 963 (2014)

Plasma spectroscopy: Temperatures



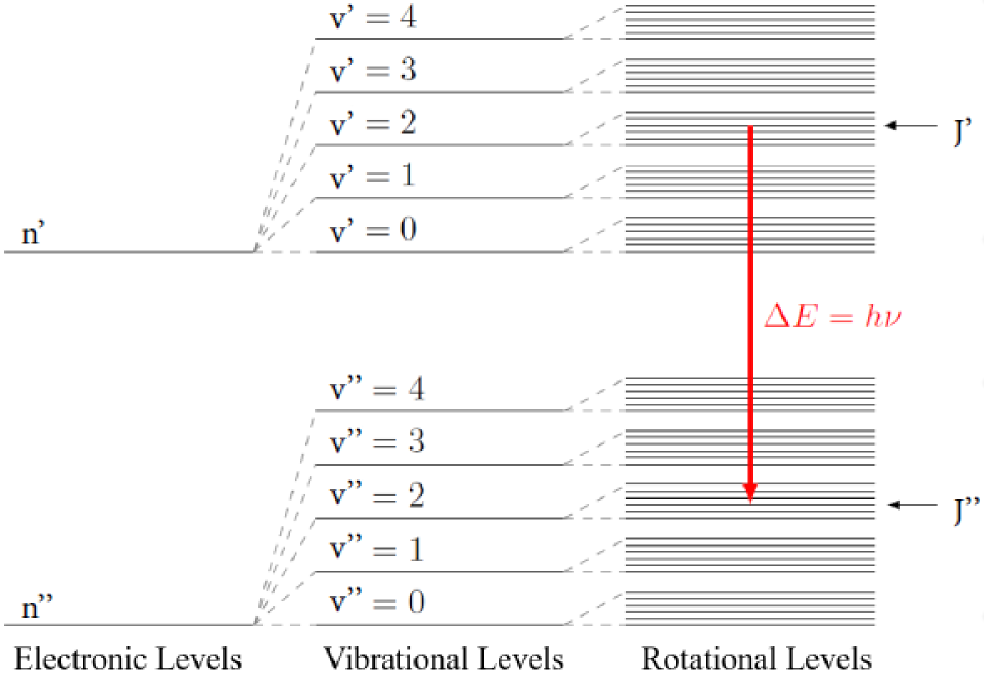
Fast cooling, but what are we really measuring ?

[Review] A. Kanitz et al., Plasma Sources Sci. Technol. (2019)

Plasma spectroscopy: Ro-vibrational spectroscopy

$AlO(B^2\Sigma^+) \longrightarrow AlO(X^2\Sigma^+)$

visible light (~ 500 nm)



Emission spectroscopy:

Population of the excited state

… from “freshly” produced molecules

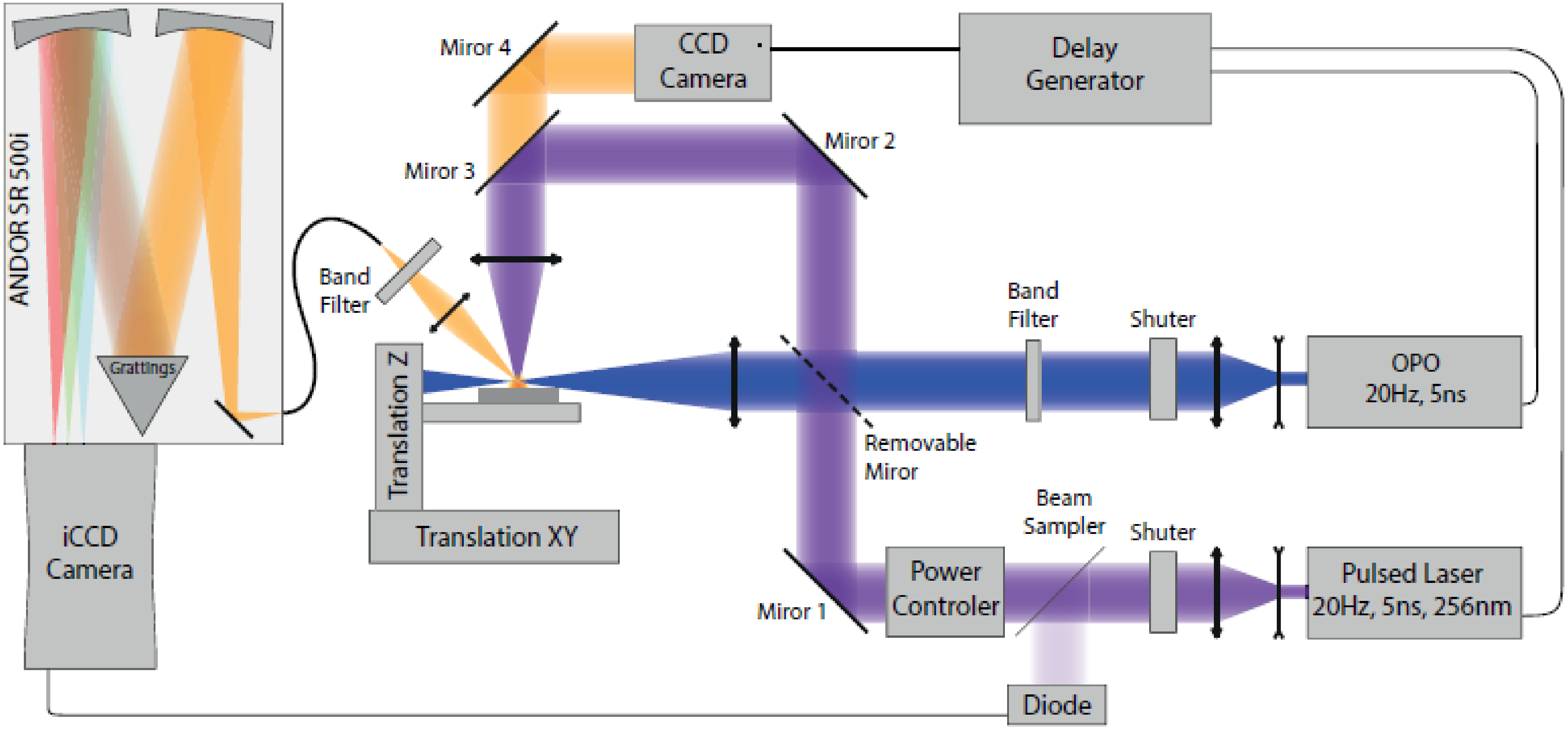
$$\mathrm{Al} + \mathrm{O} \underset{\text{desorption}}{\overset{\text{sticking}}{\rightleftarrows}} \mathrm{AlO}^* \xrightarrow{\text{cooling}} \mathrm{AlO}(B^2\Sigma^+)$$

Quenching collision

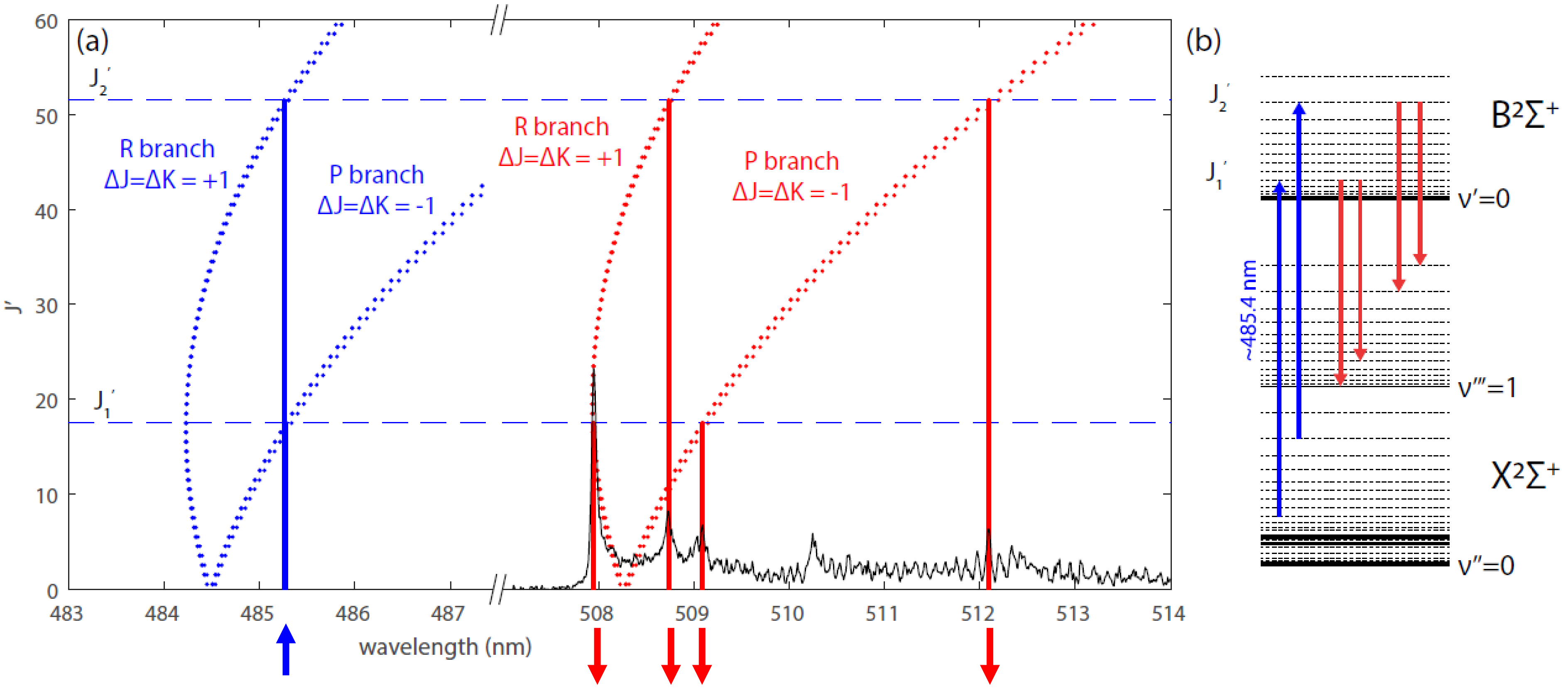
Population of the ground state certainly map the kinetic temperature.

To access the population of the ground electronic state… LIF is needed

Probing AlO(X): LIF Spectroscopy



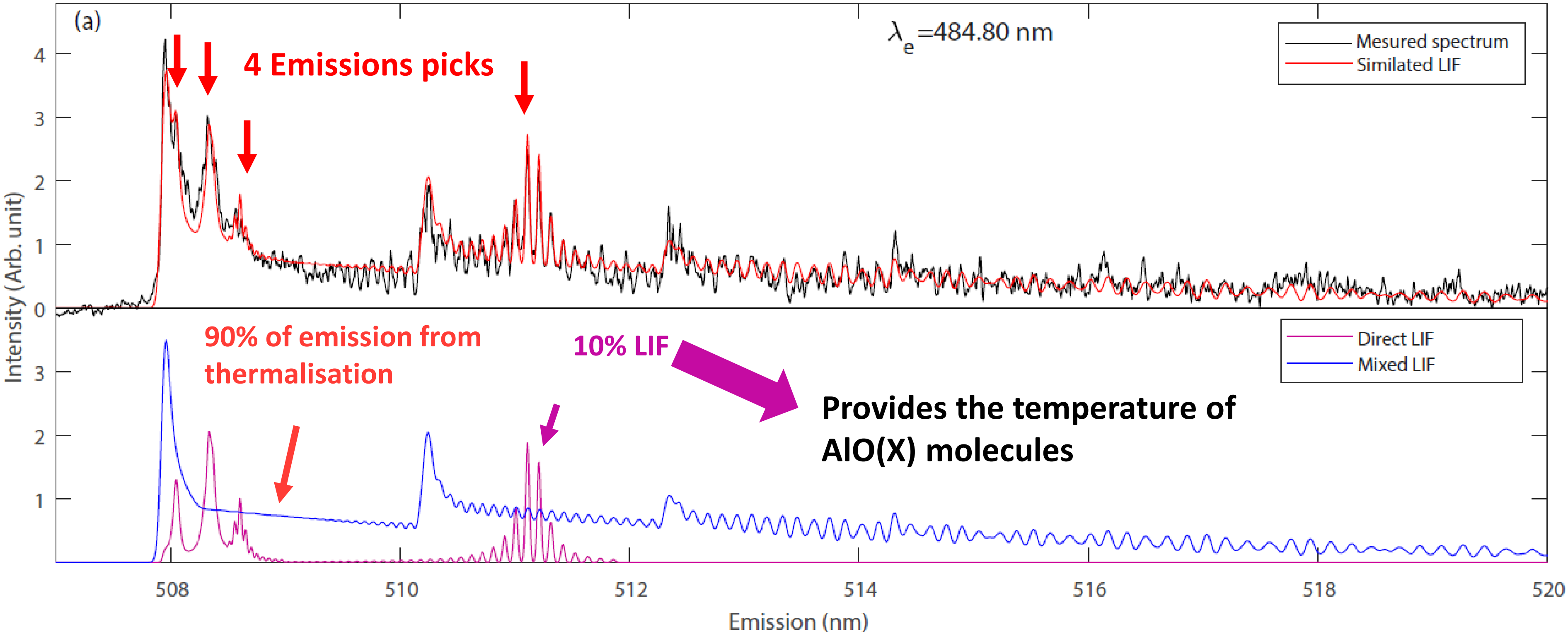
Plasma spectroscopy: Temperatures



1 Excitation

4 Emissions picks

Plasma spectroscopy: Temperatures



4 Emissions picks

90% of emission from thermalisation

10% LIF

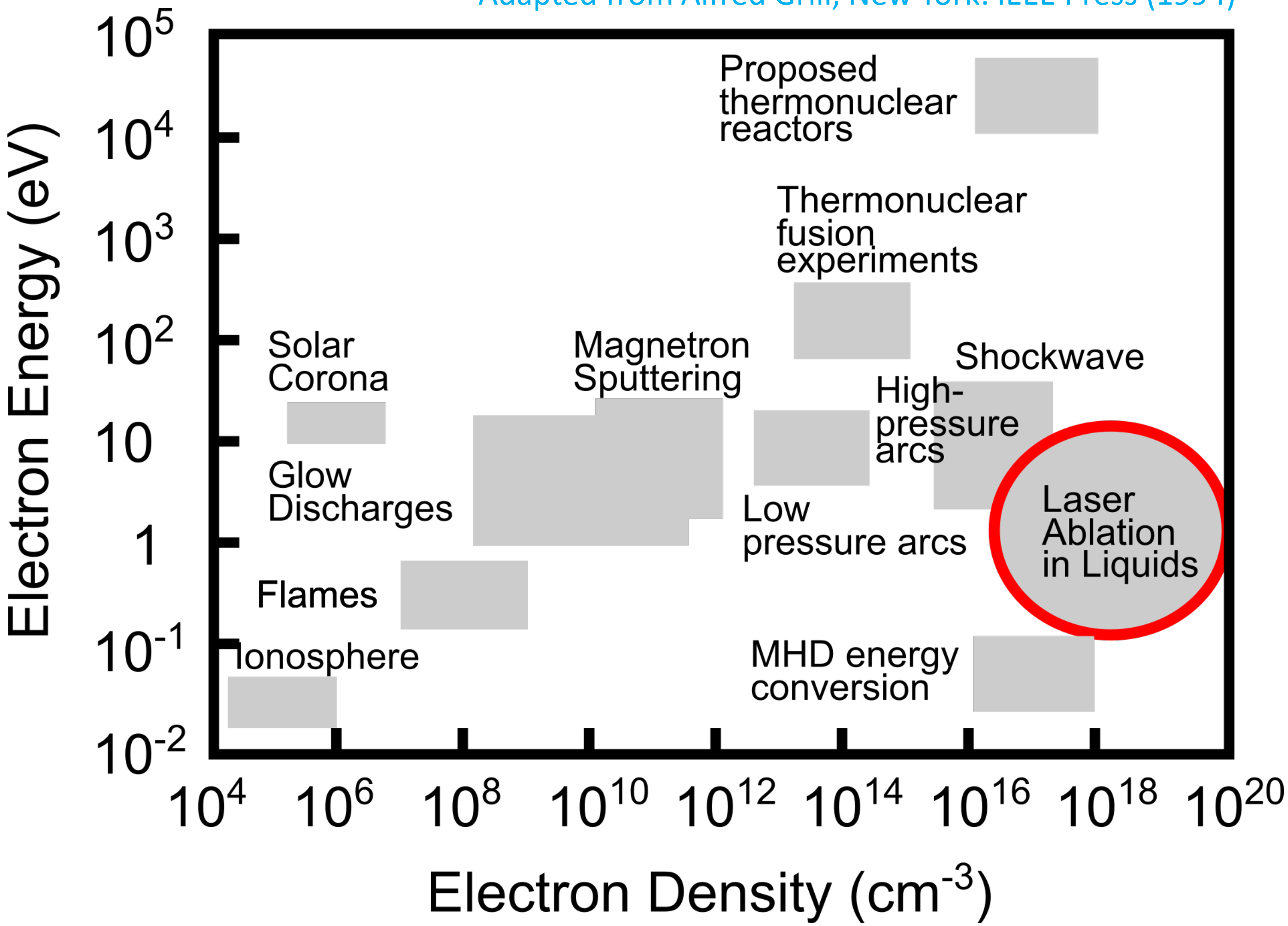
Provides the temperature of AlO(X) molecules

Delay	Trot AlO(B)	T AlO(X)
5 µs	3845 ± 75 K	3702 ± 61 K
30 µs	3130 ± 75 K	3153 ± 64 K

Ablation in air

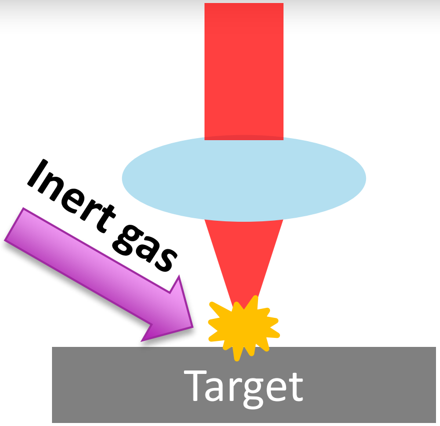
Classification of plasmas

Adapted from Alfred Grill, New York: IEEE Press (1994)



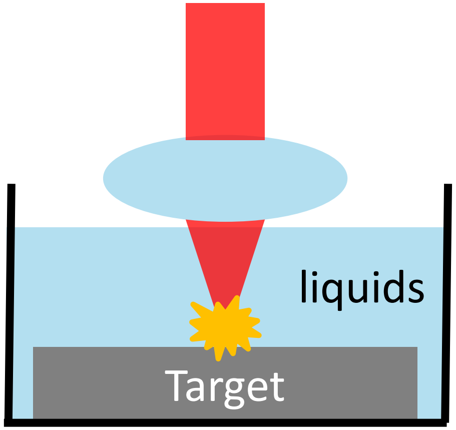
[review] A Kanitz et al., Plasma Sources Sci. Technol. 28, 103001 (2019)

Plasma spectroscopy: LIBS underwater ?



From gas to liquid

Lower electronic temperature
Shorter lifetime
Molecules appear early

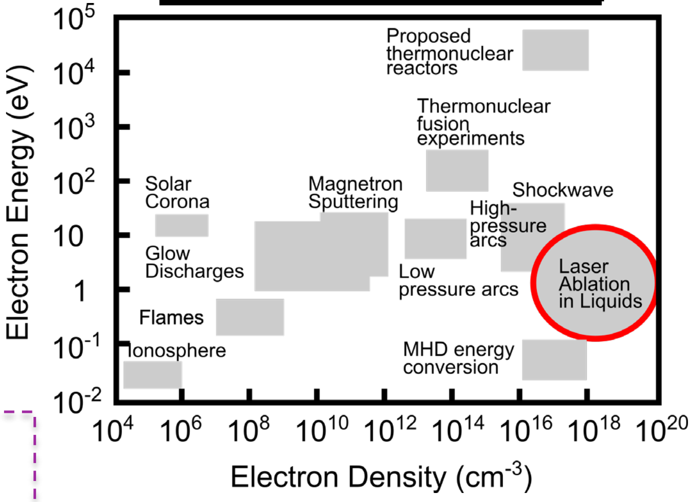


For analytical technique (LIBS like)

\+ high electron density ⟶ LTE for the electronic states

$$N_e \geqslant 6.5\times10^{16}\times\frac{g_{max}}{g_{min}}\left(\frac{\Delta E}{E_1^H}\right)^3\left(\frac{kT_{elec}}{E_1^H}\right)^{0.5}\Phi_1\left(\frac{\Delta E}{kT_{elec}}\right)$$

H. Drawin, Zeitschrift fur Physik, 1969, 228, 99.



- Low temperatures ⟶ partial information, i.e. some species are not excited (H, ions, OH…).
- Molecules: observed at delay = 0 / excitation mechanism ?

~ Plasma homogeneity ?

~~LIBS~~

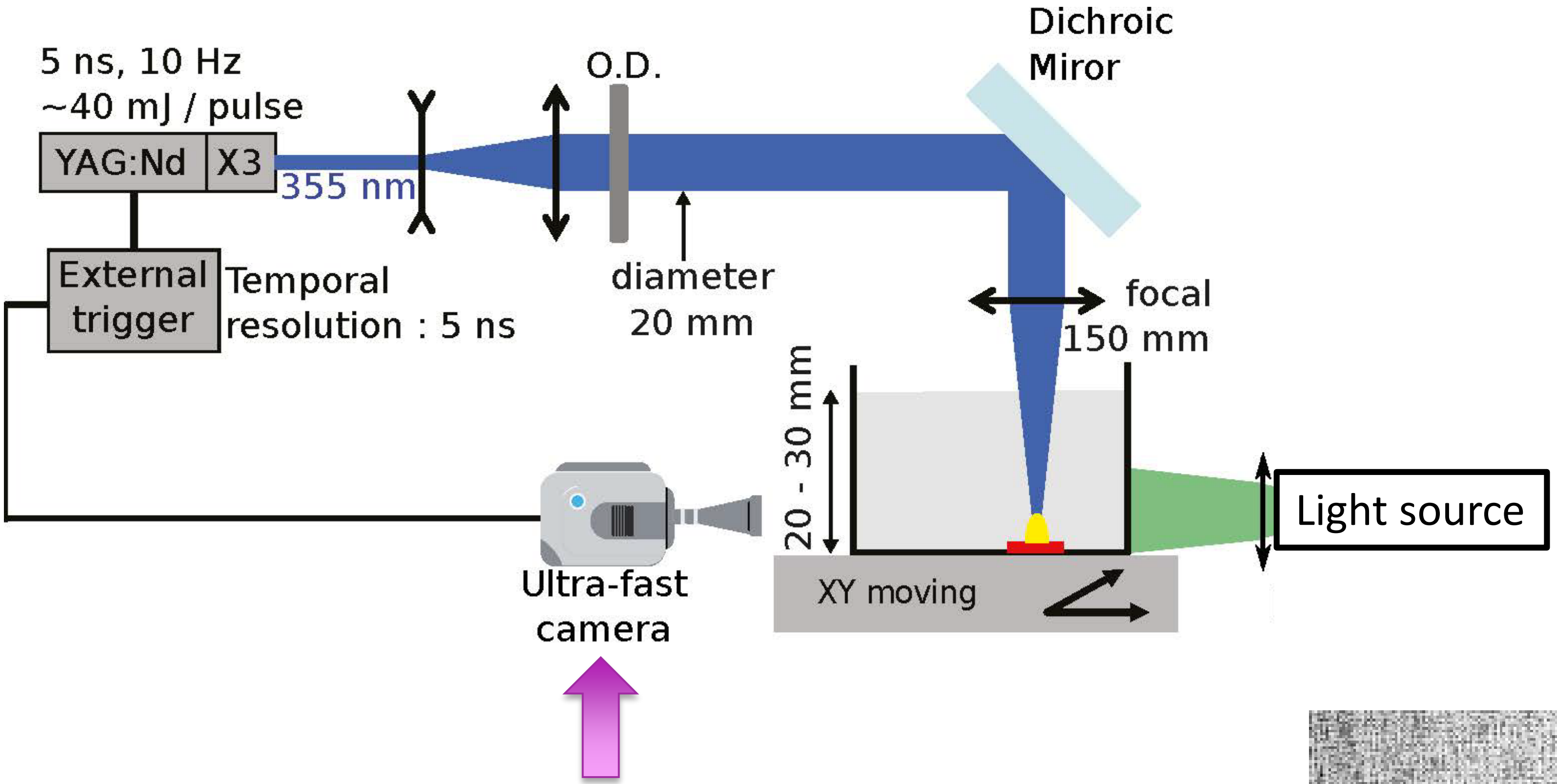
Next step: Delayed double-pulse excitation

See bibliography of A. De Giacomo @ Univ. of Bari

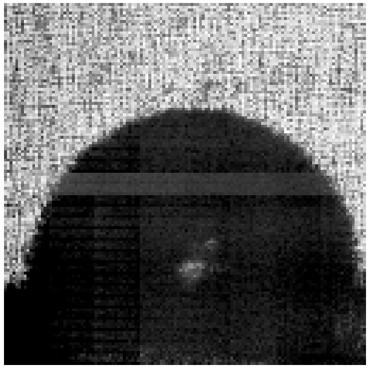
Bubble dynamics

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

Bubble dynamics

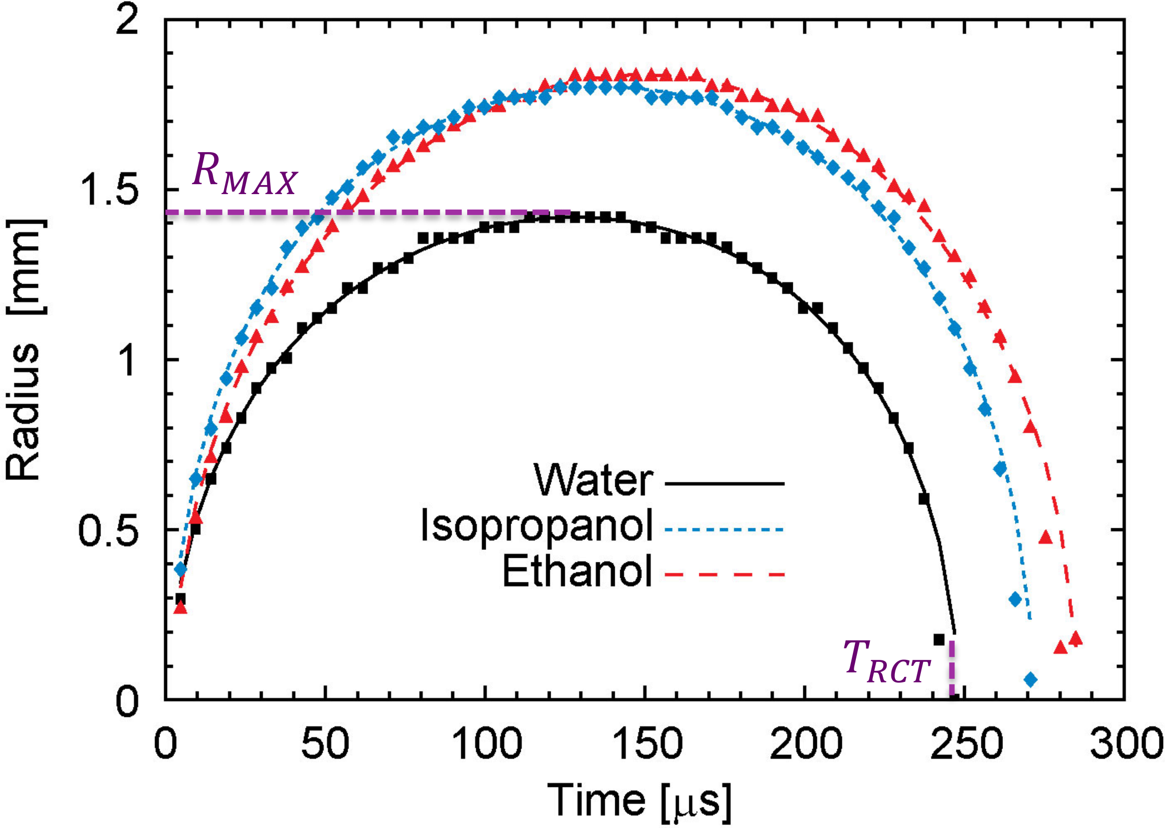


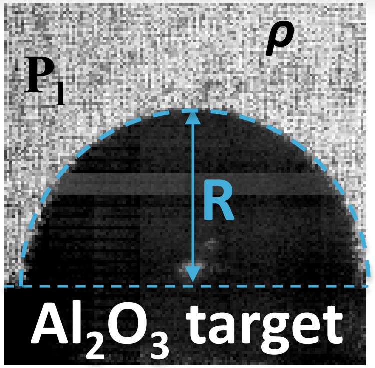
Camera Phantom v711 from
Vision Research
Zoom 6000 from Navitar
Frame rate 210000 fps

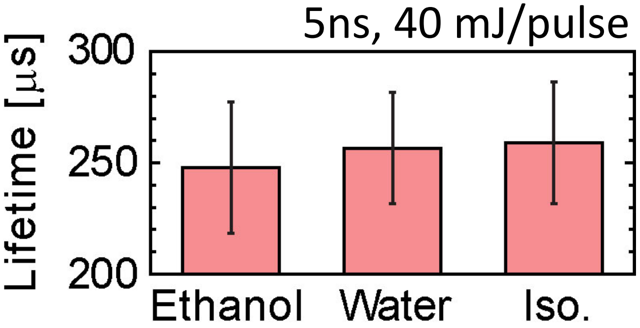


Bubble dynamics

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







Rayleigh collapse time:

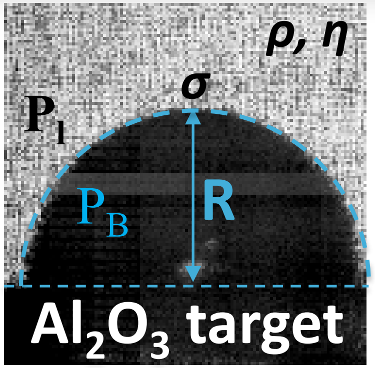
$$T_{RCT} = 1{,}83\, R_{MAX} \sqrt{\frac{\rho}{P_l}}$$

J. Lam *et al.*, Appl. Phys. Lett. **108**, 074104 (2016)

Bubble dynamics

Rayleigh-Plesset (RP) equation

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



σ fluid surface tension

ρ liquid mass density

η dynamic viscosity

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

Relative contribution of each term :

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

Weber number $\mathcal{W}e = \rho\dot{R}^2R/\sigma \simeq 1\times10^2.$

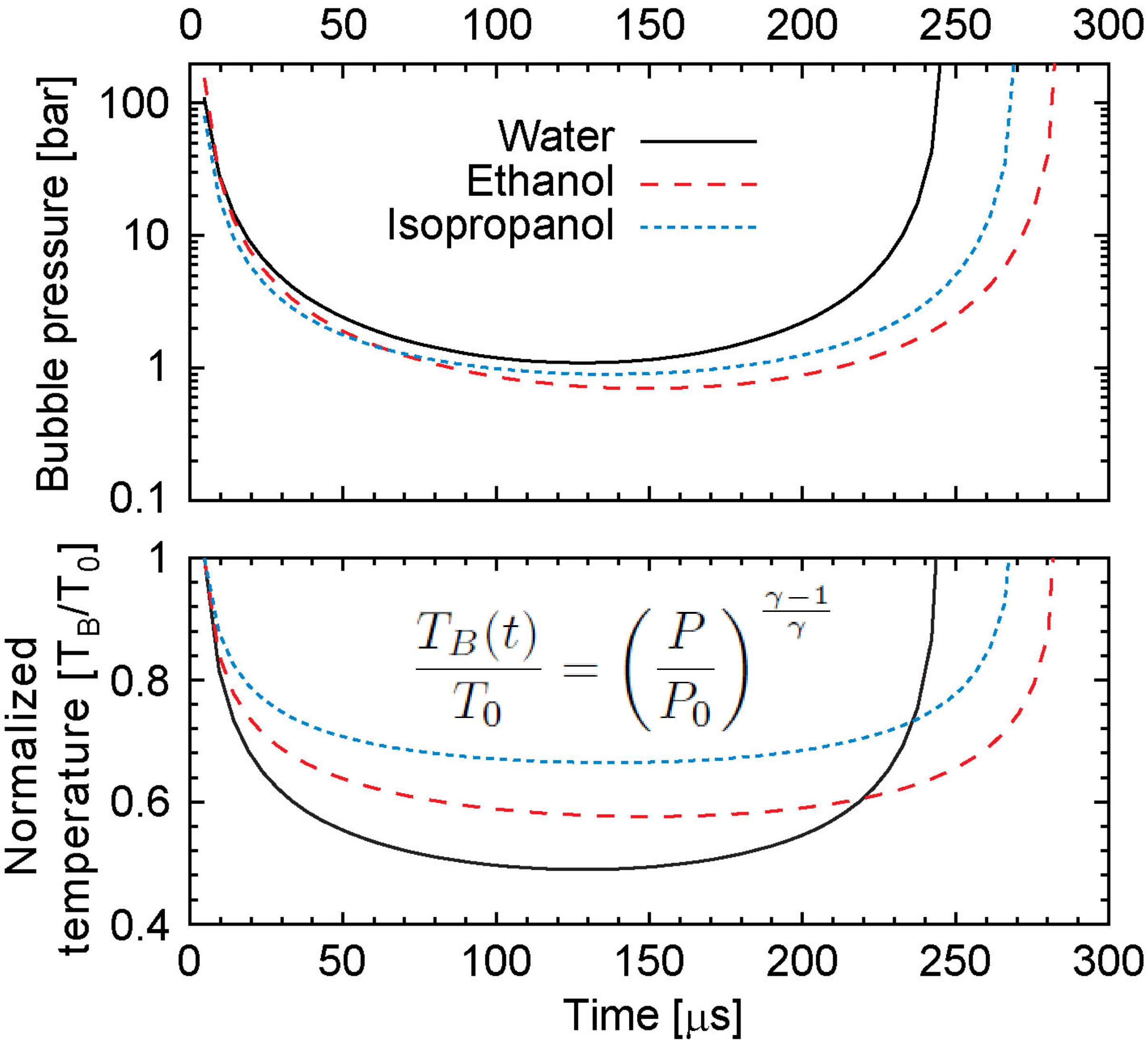
Reynolds number $\mathcal{R}e = \rho\dot{R}R/\eta \simeq 3\times10^3$

The surface motion of the bubble is driven by inertial forces

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

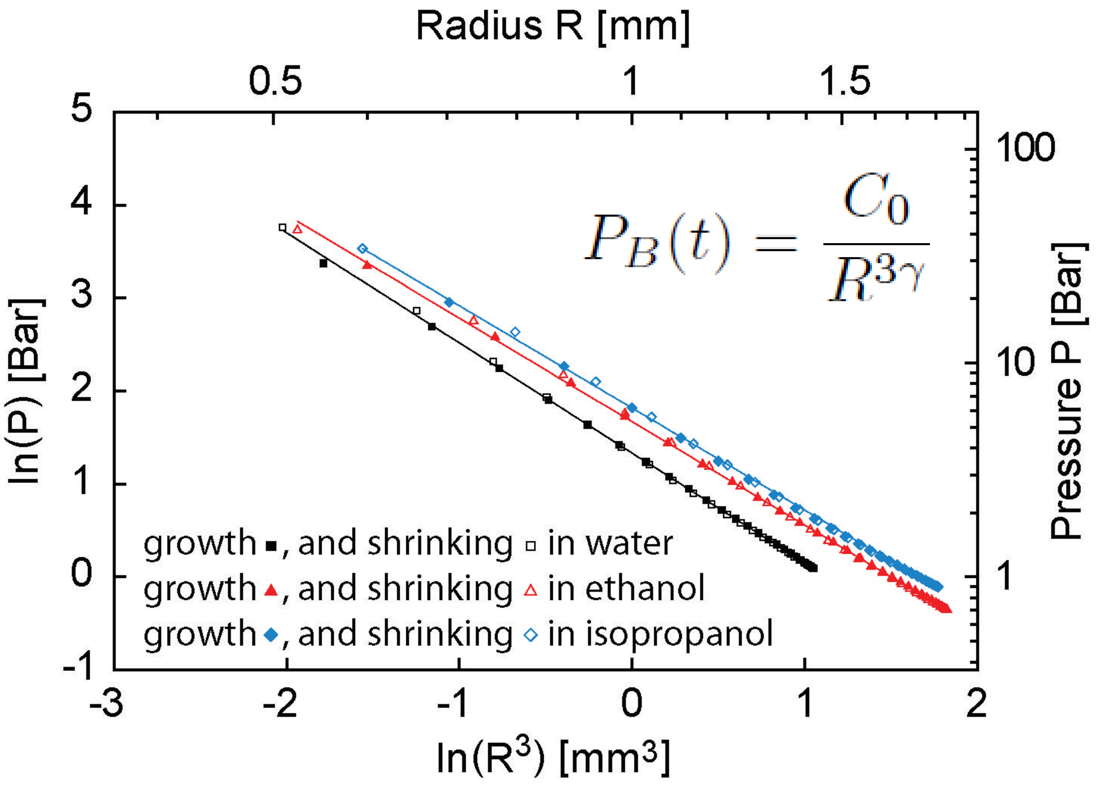
$$\rho(R\ddot{R} + \frac{3}{2}\dot{R}^2) = P_B(t) - P_l$$

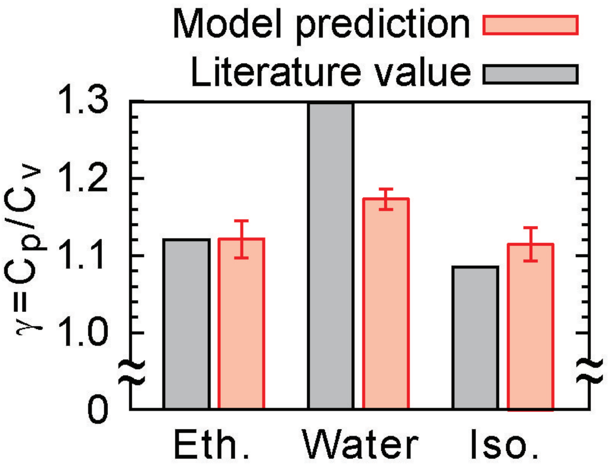
Bubble dynamics

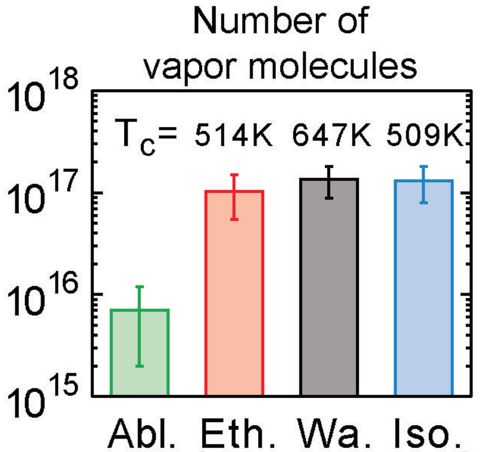


$$\frac{T_B(t)}{T_0} = \left(\frac{P}{P_0}\right)^{\frac{\gamma-1}{\gamma}}$$

Isentropic process !







Adiabatic ?

R ≈1 mm, h ≈ 100 W/m²/K, T_c ≈ 650 K

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

300 µs → 0,1 mJ

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

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.

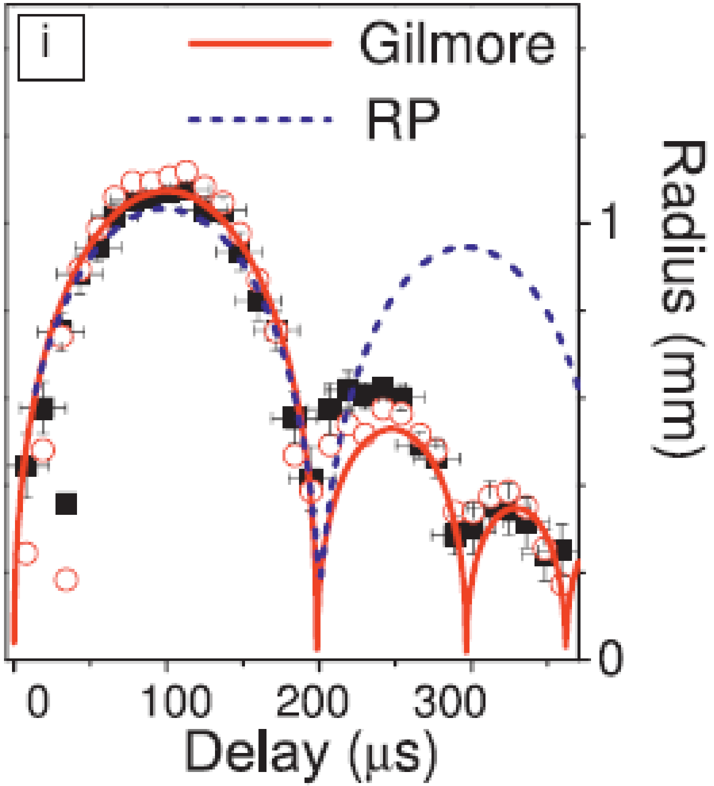
Considers: liquid compressibility, viscosity and surface tension.

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

$$\frac{P+B}{p_\infty+B}=\left(\frac{\rho}{\rho_0}\right)^n$$

Water: B = 314 MPa, n=7



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

A. Vogel et al., J. Acoust. Soc. Am. 100, 148 (1996).

Bubble dynamics

**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_∞

$$H=\int_{p_\infty}^{P(R)}\frac{dp}{\rho}$$

p and *p* are the density and pressure within the liquid

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

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

κ 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

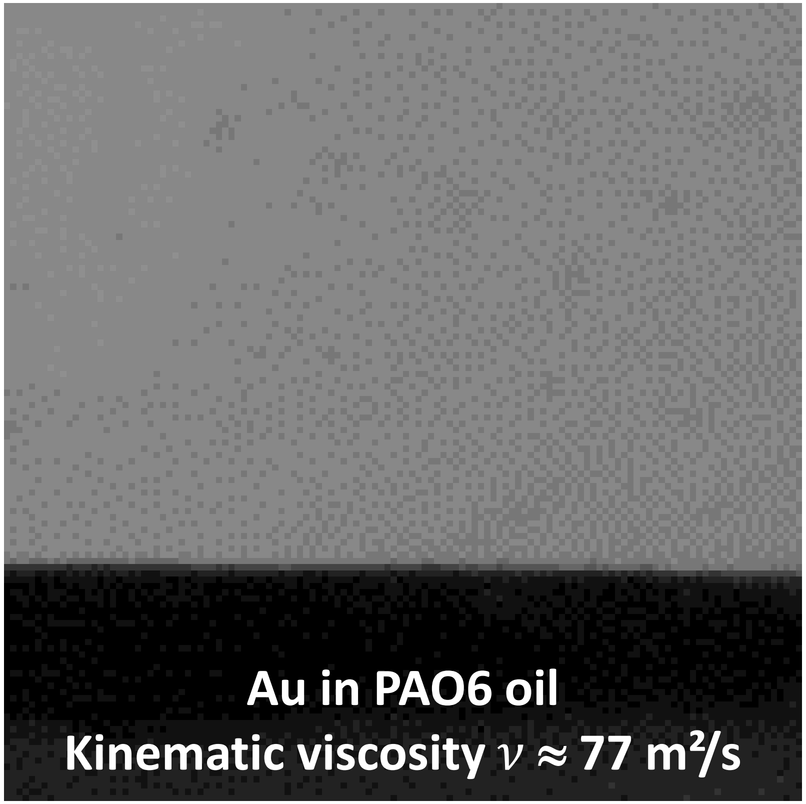
Assuming Tait’s equation ➔

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

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

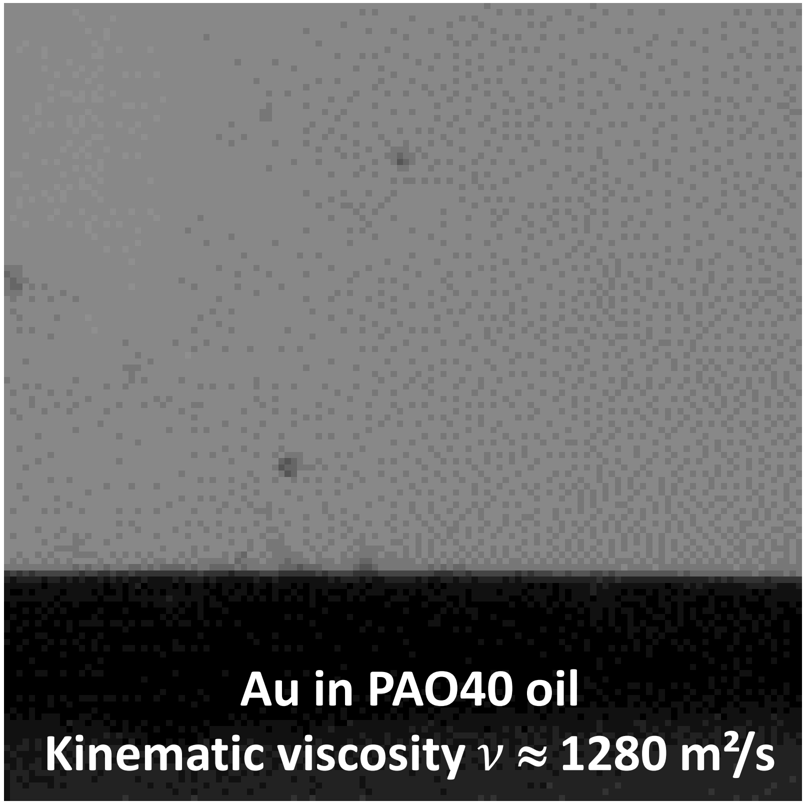
A. Vogel et al., J. Acoust. Soc. Am. 100, 148 (1996).

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



Au in PAO6 oil

Kinematic viscosity $\nu \approx 77\ m^2/s$



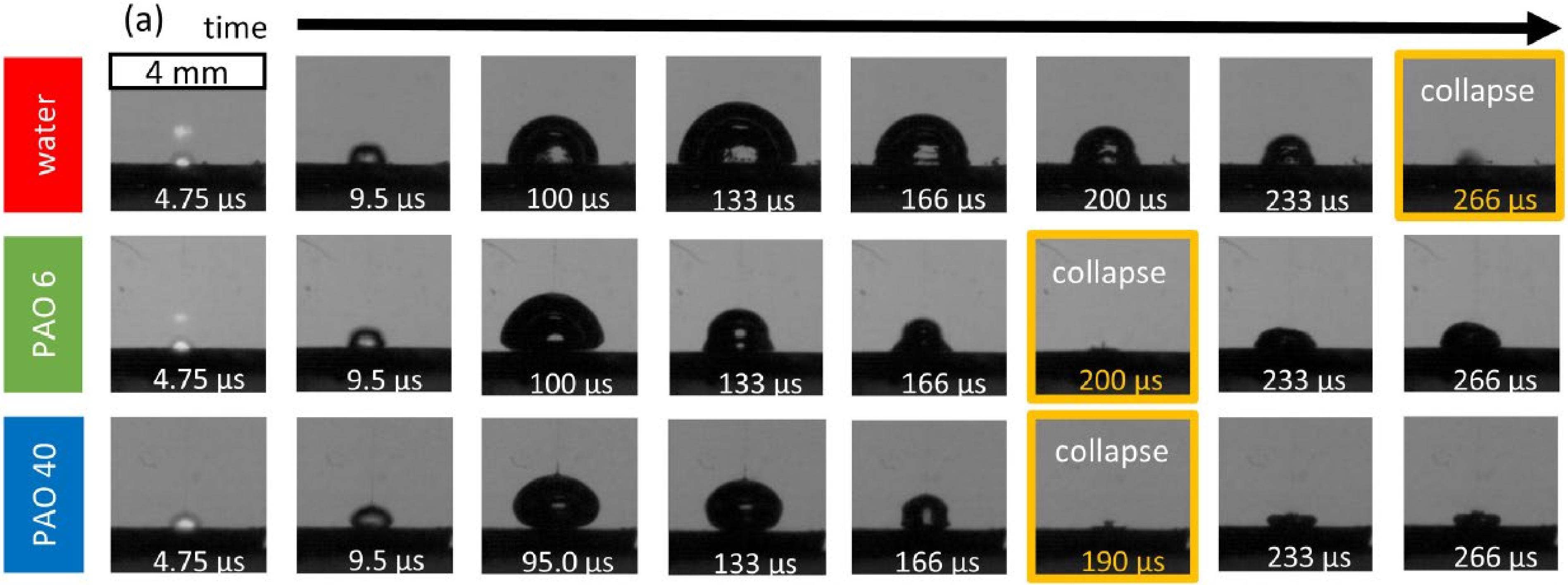
Au in PAO40 oil

Kinematic viscosity $\nu \approx 1280\ m^2/s$

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

T. Hupfeld et al., J. Appl. Phys. 127, 044306 (2020)

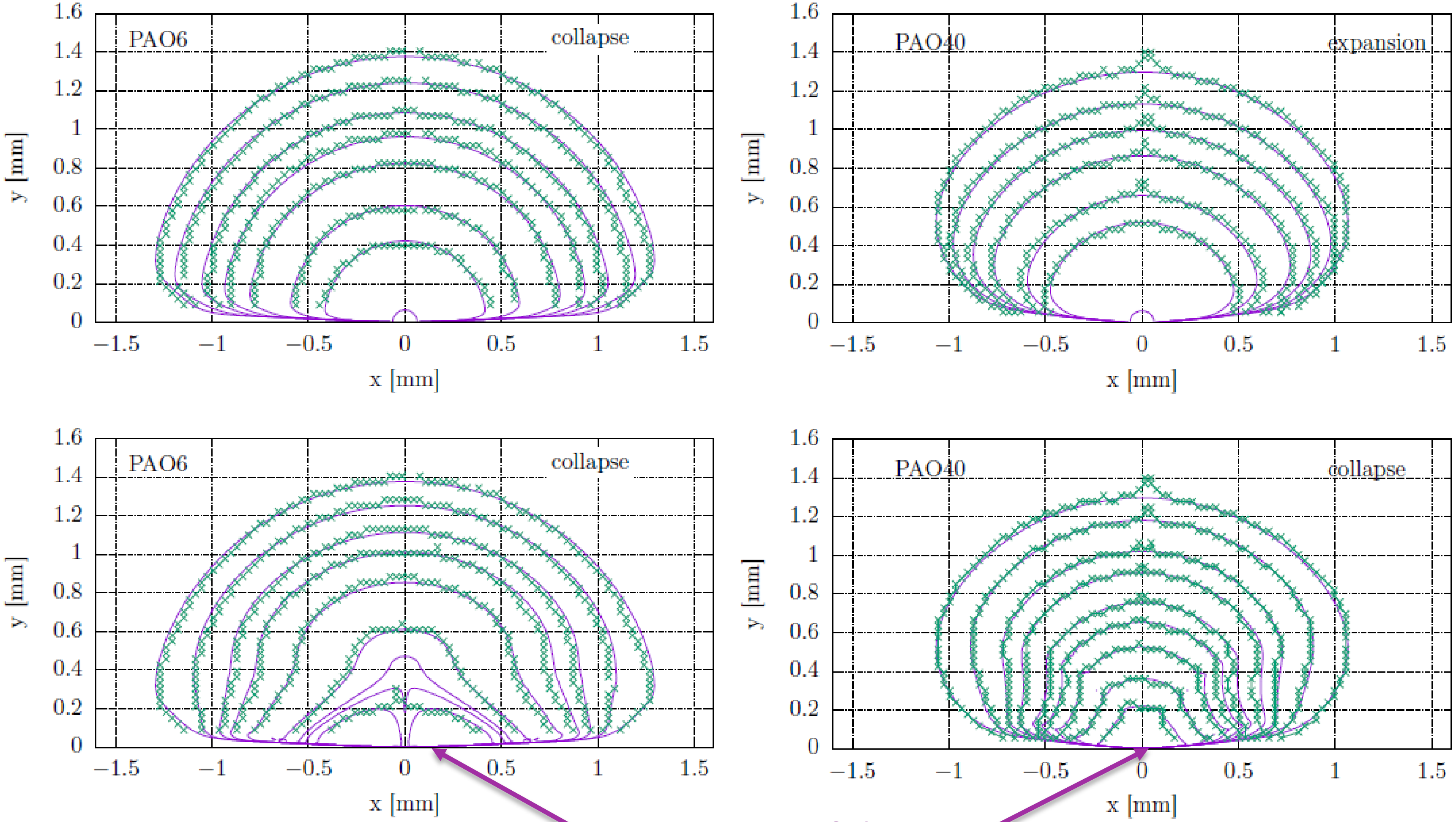
Ablation in viscous liquids : poly-*alpha*-olefin (PAO)



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

T. Hupfeld et al., J. Appl. Phys. 127, 044306 (2020)

Direct resolution of the continuity and Navier-Stokes equations
(Finite volume method, *OpenFOAM* open source software @ https://www.openfoam.com/)



Suppression of the jet

M. Koch et al., Comput. Fluids 126, 71 (2016)
C. Lechner et al., Phys. Rev. Fluids, 2020, 5, 093604.

Contents

Characteristic time scales in laser ablation

Shock waves

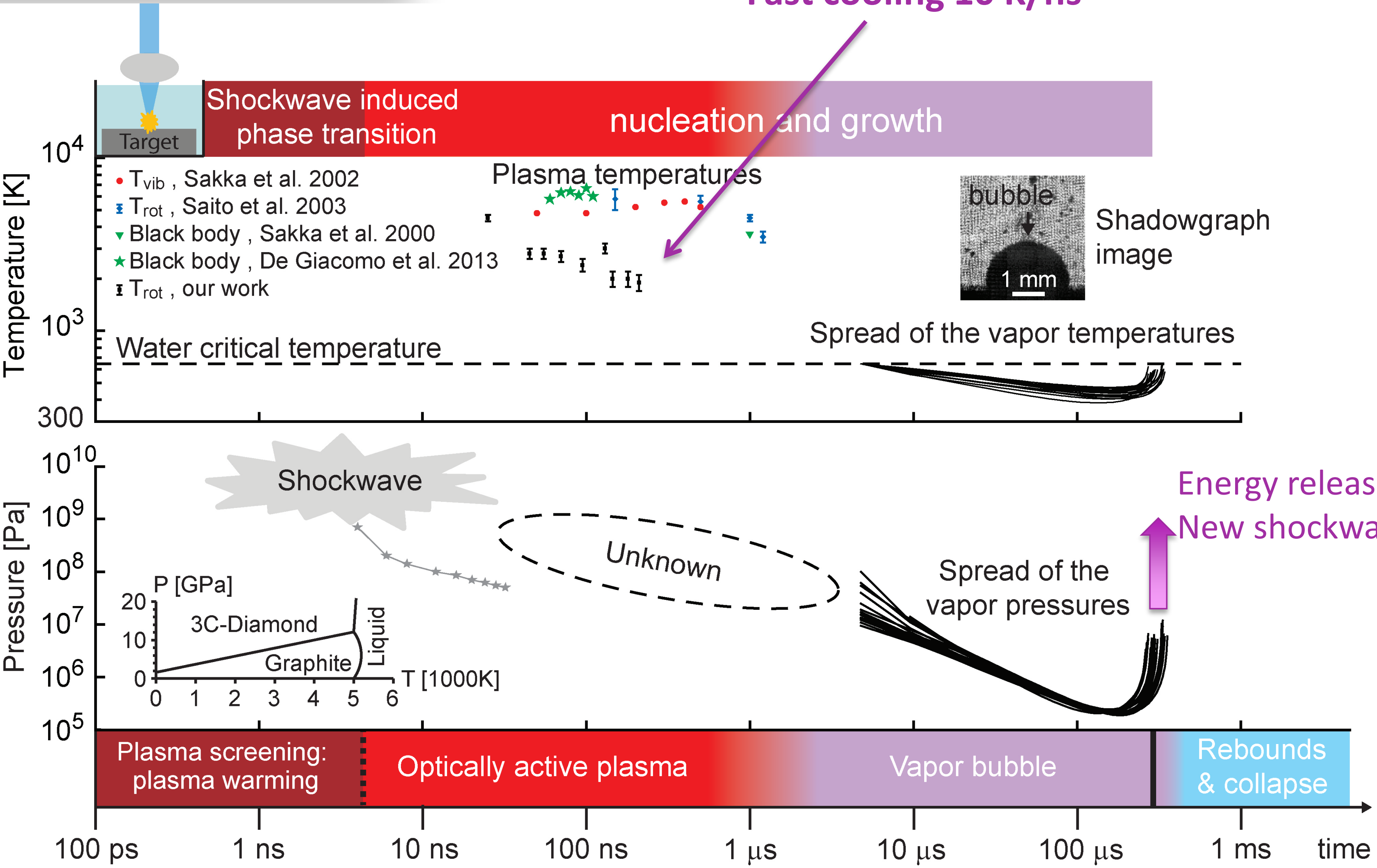
Plasma spectroscopy

Bubble dynamics

A few words on laser generation of colloids

Thermodynamic parameters

Fast cooling 10 K/ns

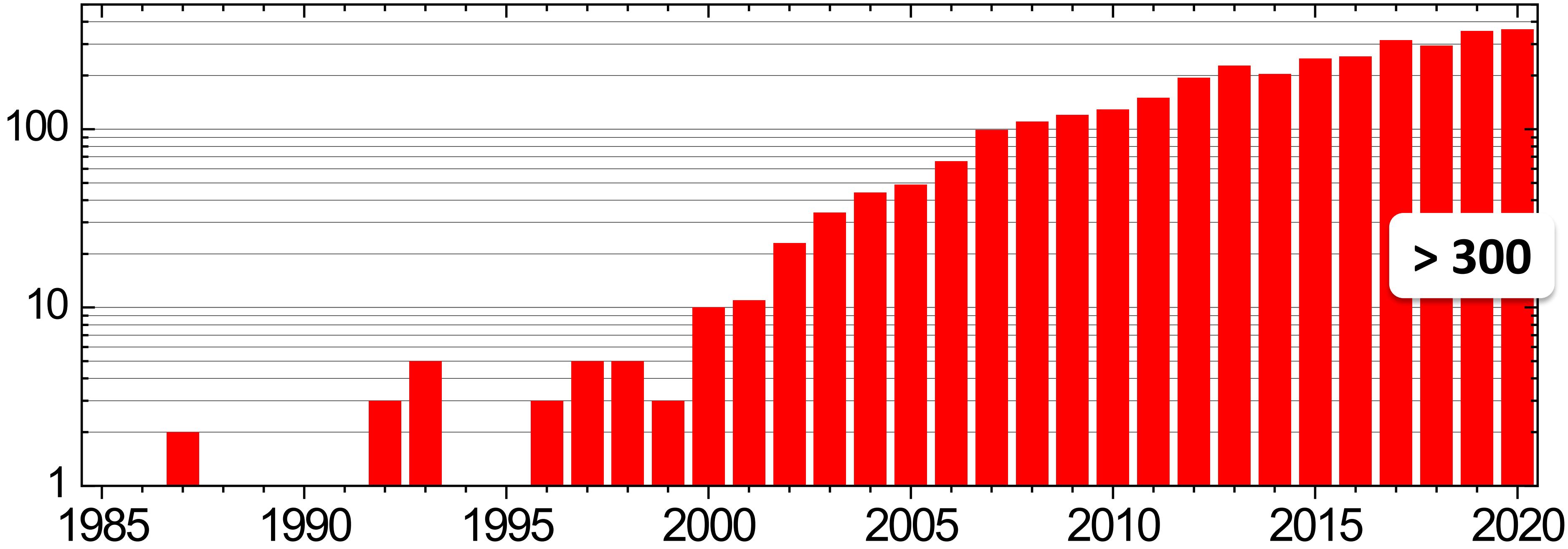


Energy release : New shockwave

D. Amans *et al.*, Origin of the nano-carbon allotropes in pulsed laser ablation in liquids synthesis, J. Colloid Inter. Sci. **489**, 114-125 (2017).

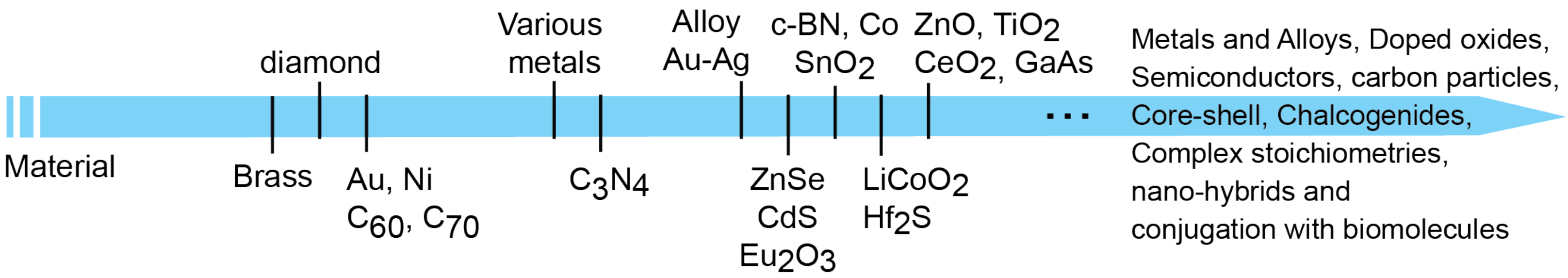
Contents

Laser generation of colloids



Publication count

> 300



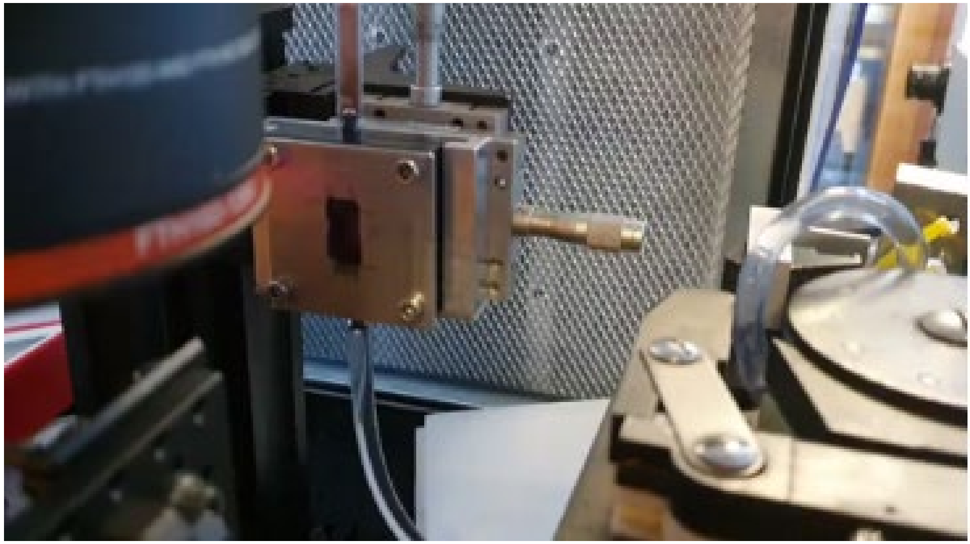
Material

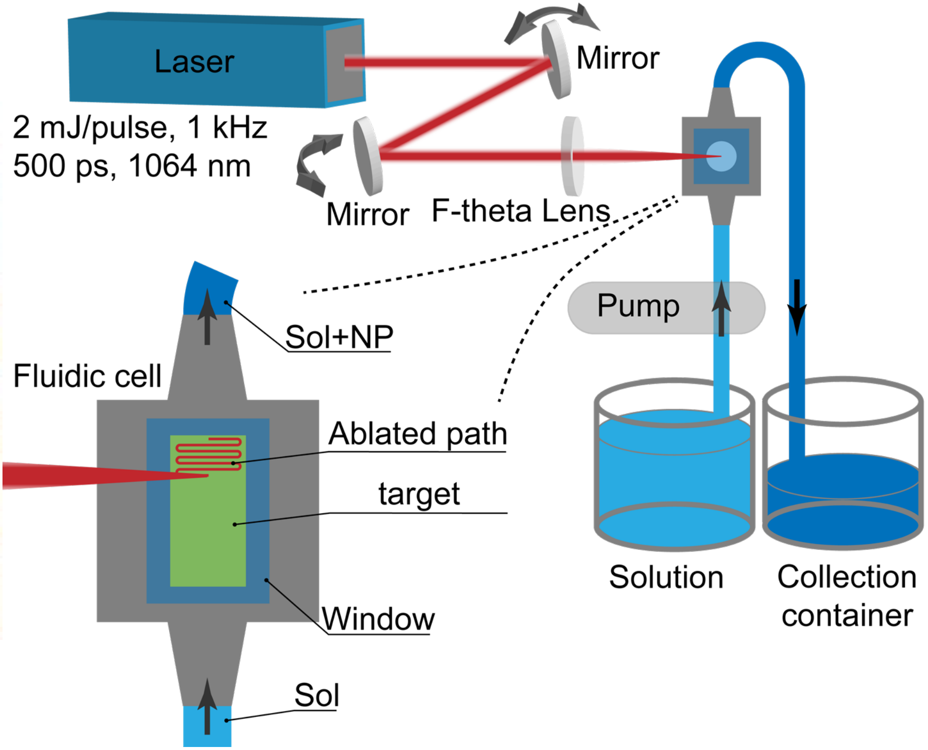
diamond
Brass
Au, Ni
C_{60}, C_{70}
Various metals
C_3N_4
Alloy Au-Ag
ZnSe
CdS
Eu_2O_3
c-BN, Co
SnO_2
LiCoO_2
Hf$_2$S
ZnO, TiO_2
CeO_2, GaAs
. . .

Metals and Alloys, Doped oxides, Semiconductors, carbon particles, Core-shell, Chalcogenides, Complex stoichiometries, nano-hybrids and conjugation with biomolecules

Versatility of the method + new approach: Laser Ablation in Liquids (LAL), Laser Melting in liquids (LML), Laser Fragmentation in Liquids (LFL).

Continuous flow setup

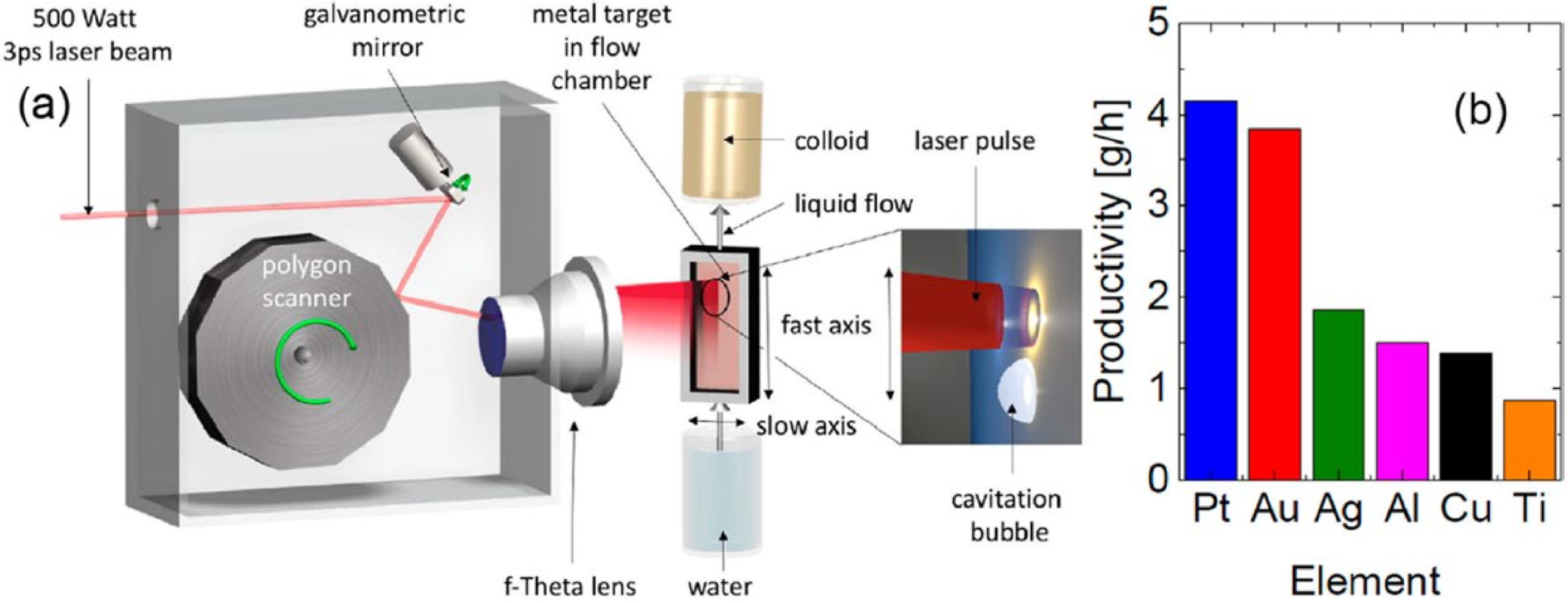




Productivity 15 – 40 mg/hour

Laser generation of colloids

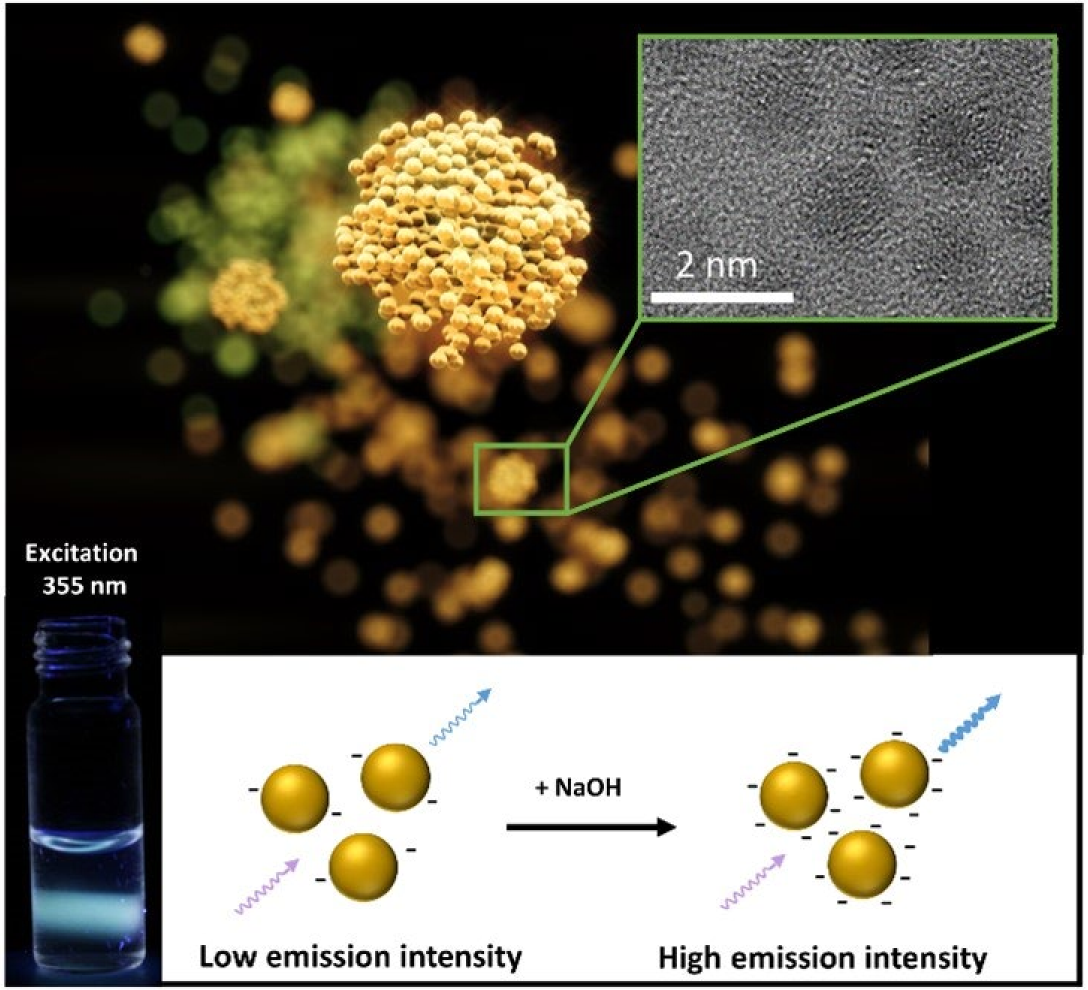
Higher productivity using high repetition rate lasers



R. Streubel *et al.*,, Opt. Lett. **41**, 1486−1489 (2016). / R Streubel *et al.*, *Nanotechnology* **27**, 205602 (2016).

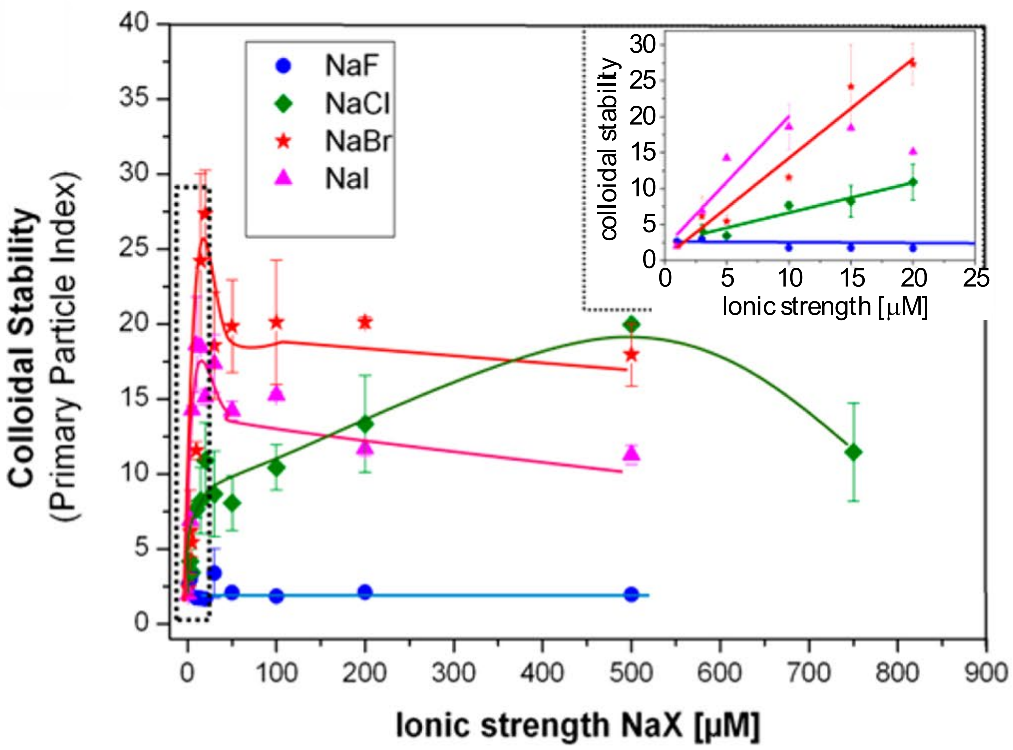
Laser generation of colloids

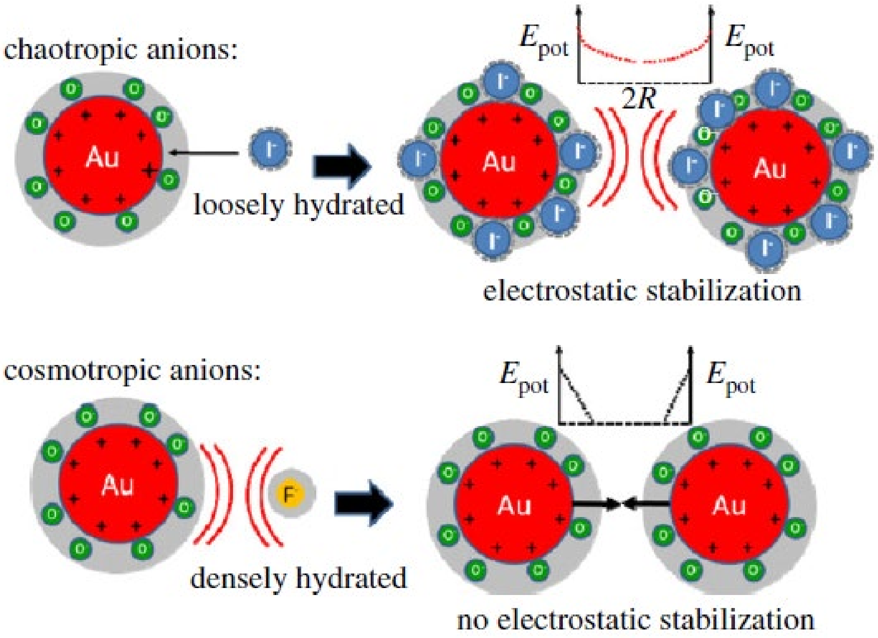
Ligand free clusters produced by laser fragmentation



A. R. Ziefuss et al., Advanced Materials (2021), https://doi.org/10.1002/adma.202101549

Size & stability control : Halide anions





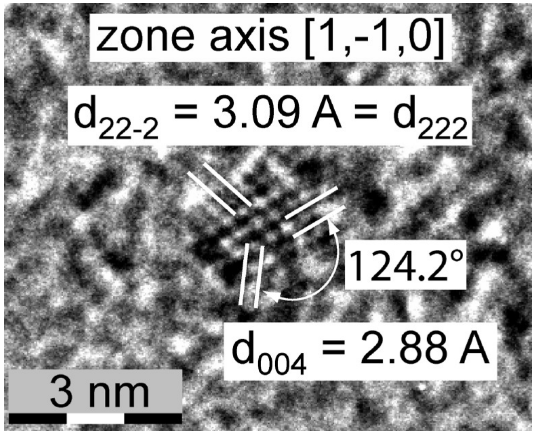
Ligand Free !

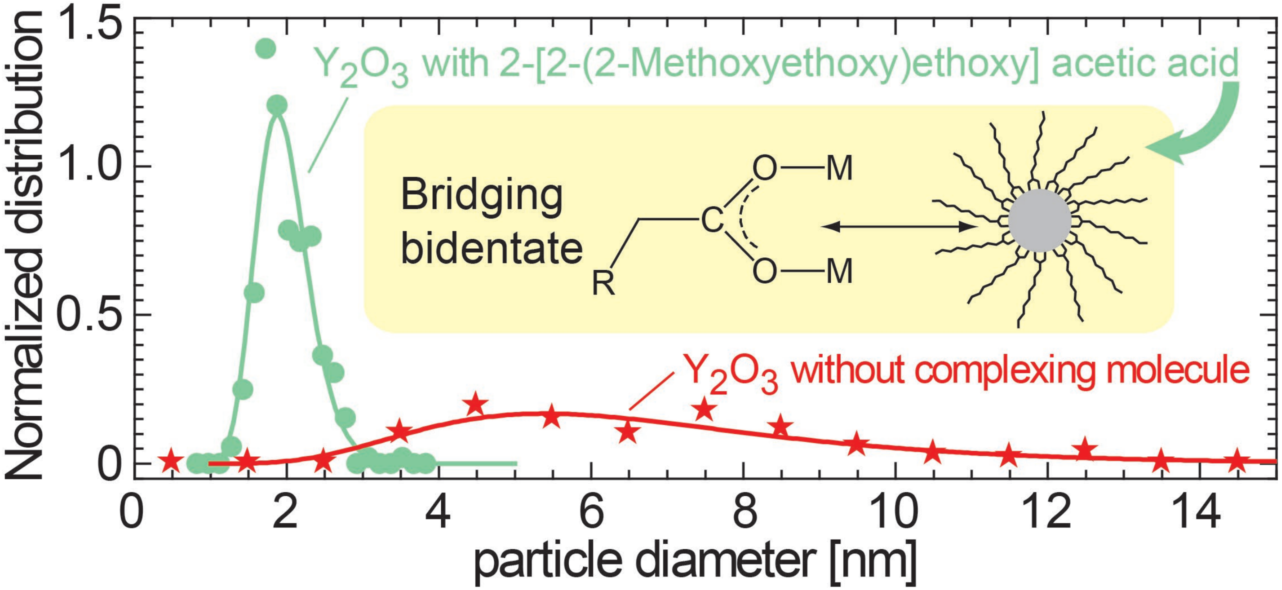
V. Merk *et al.*, Langmuir **30**, 4213 (2014).
C. Pfeiffer et al,, J. R. Soc. Interface. **11**, 20130931 (2014).

Laser generation of colloids

Size control using ligands

Gd_2O_3

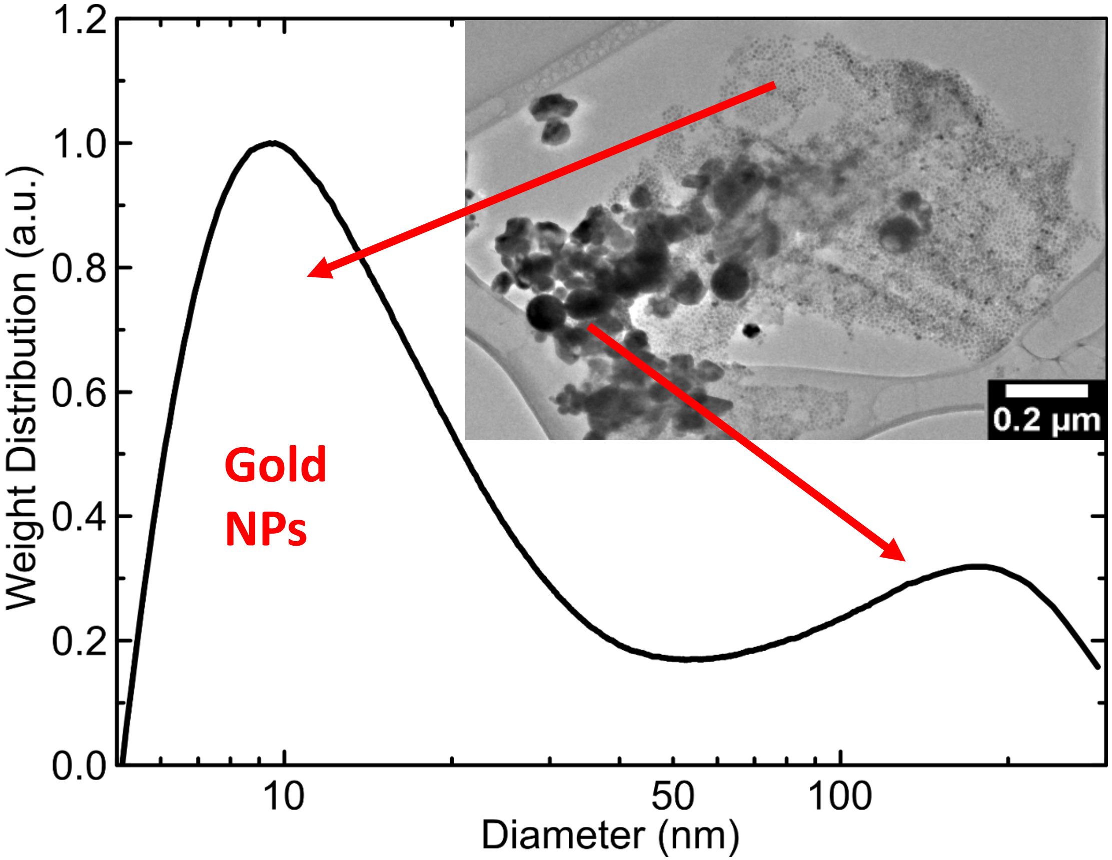




D. Amans et al., J. Phys. Chem. C 115, 5131–5139 (2011)

Main drawback of ligand-free nanoparticles

- Binomial size distribution
- Shape

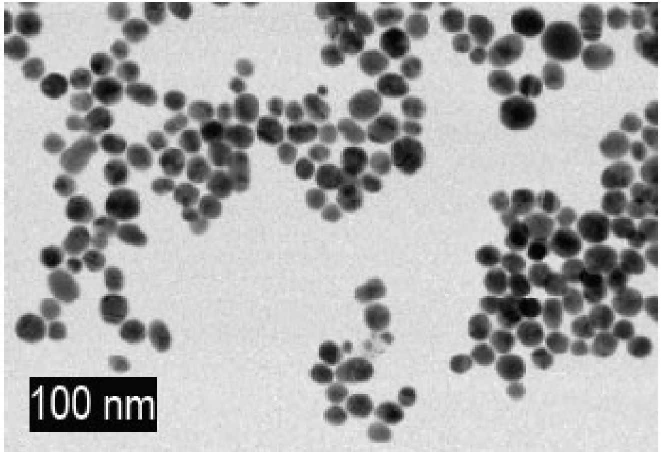


Manufacturers

I-colloid

from **IMRA**
Pioneering Ultrafast Fiber Laser Technology

Gold nanoparticles 20nm



O.D.	Volume	Price
5	50 mL	$325
5	100 mL	$400

STREM
Reactant & Surfactant-free pure Nanoparticles via Laser Ablation
Particular customized material

metals · inorganics · organometallics · catalysts · ligands · custom synthesis · cGMP facilities · nanomaterials

What is Laser Ablation?

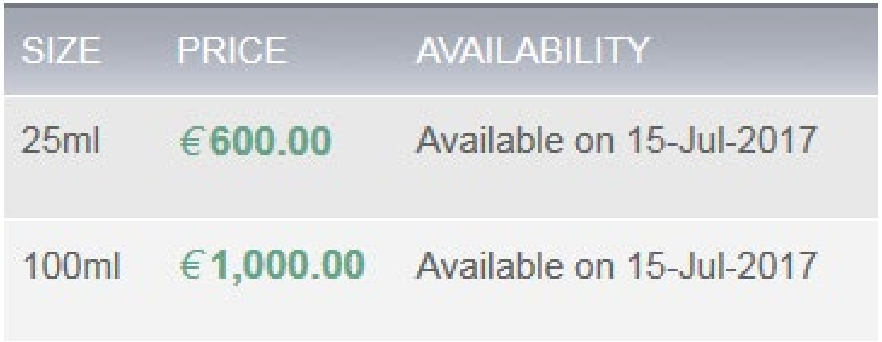
Laser ablation is a physical process used to generate nanoparticles. It involves the use of short pulses of laser energy focused on a target in a solvent. The target absorbs the energy from the laser pulse and is vaporized. The vaporized material then condenses as nanoparticles.

Why Laser Ablation?

Laser ablation generates nanoparticle dispersions that are free of any contaminants, such as unreacted starting materials.

Basic process of pure, physical laser ablation in liquids, demonstrated at a gold foil in an open glass vessel. [For production, Particular uses ablation chambers instead]

- **Gold nanoparticles < 20nm,**
- **In water at 500mg/L (O.D.5)**
- **Surfactant and reactant-free, Stabilized with < 0.01 mmol/l of citrate**



SIZE	PRICE	AVAILABILITY
25ml	€600.00	Available on 15-Jul-2017
100ml	€1,000.00	Available on 15-Jul-2017

X 1,5 Chemically synthesized.

ANGEL conference

ANGEL
CONFERENCE

Advanced Nanoparticle Generation and Excitation by Lasers in Liquids

http://angel-conference.org/

Acknowledgement

Institut Lumière Matière (ILM) , Univ. Lyon 1 / CNRS, France

Collaborators: **Abdul-Rahman Allouche, Gilles Ledoux, Samy Mérabia, Vincent Motto-Ros, Christophe Dujardin.**

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