Cavity Ring-Down Spectroscopy as a Tool for Plasma Diagnostics

Nikša Krstulović

Institute of Physics, Zagreb

Croatia

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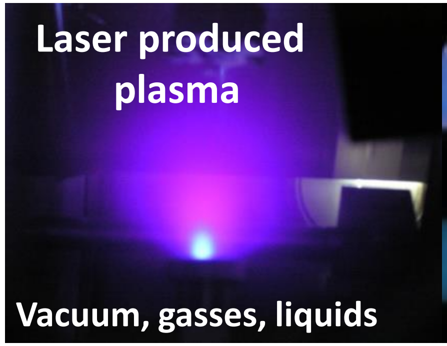
Plasma sources:

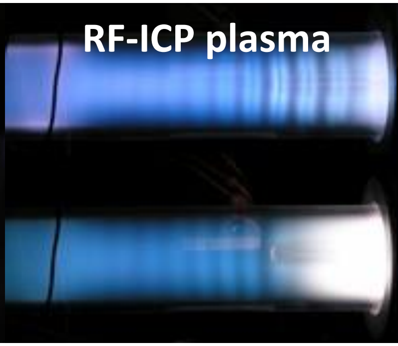
LPP – Laser Produced Plasmas

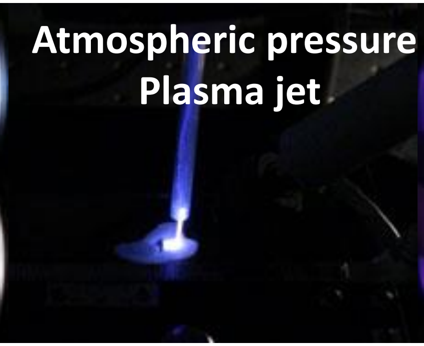
RF-ICP Plasmas (low pressure, cold)

APPJ – Atmospheric Pressure Plasma Jet (cold)

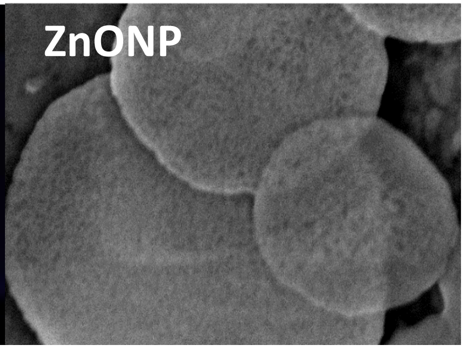

Laser produced plasma

Vacuum, gasses, liquids

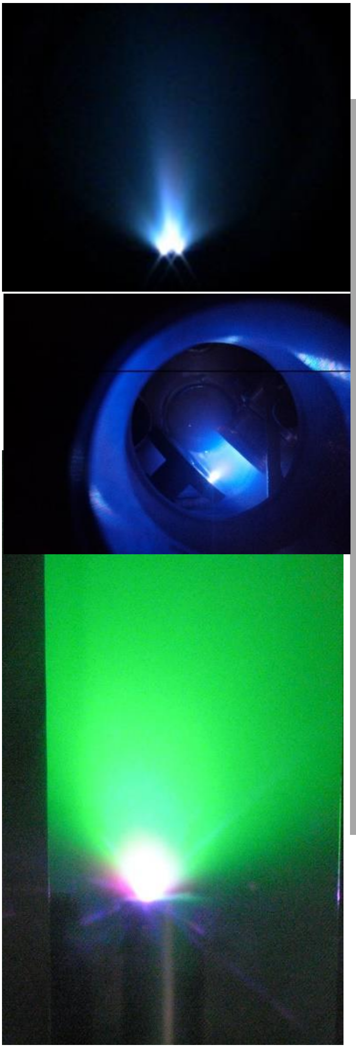

RF-ICP plasma


Atmospheric pressure Plasma jet


Plasma jet – low pressure


ZnONP

Laser Produced Plasma

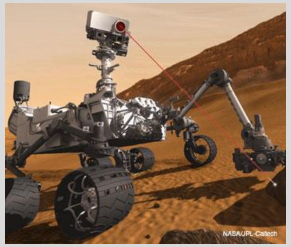


LPP as source:

- photons (EUV, XUV, X-ray)
- ions, atoms and molecules
- nanoparticles

Applications:

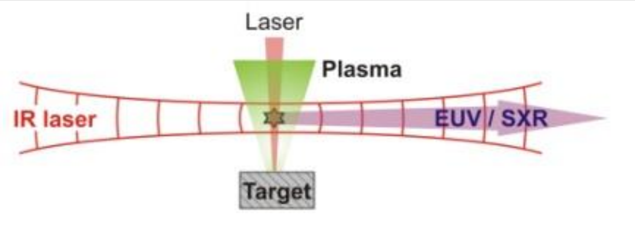
1. Laser Induced Breakdown Spectroscopy
Samples analysis and diagnostics, materials characterization



2. Pulsed Laser Deposition
Thin film production

3. EUV/XUV sources of light
Photolithography, metrology, water window (X-ray bio-imaging)

4. Medium for High Harmonics Generation
Coherent attosecond SXR pulse – table-top x-ray lasers - attosecond science



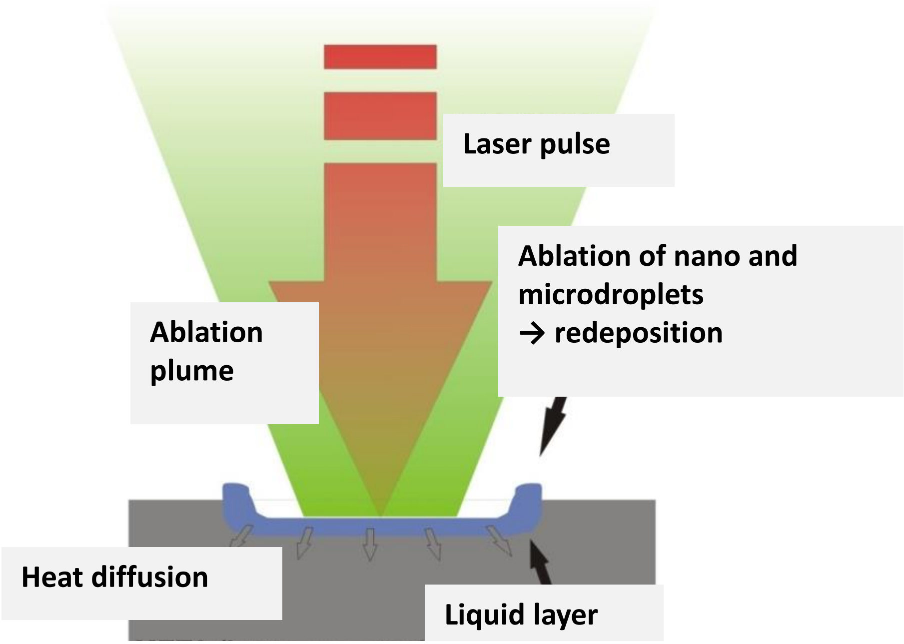
5. Nanoparticles production

6. Microstructuring

7. Plasma acceleration (ions, e^- , e^+ , p)
Table-top accelerators

Laser ablation process

(→ Mass removel by coupling laser energy to a target material)

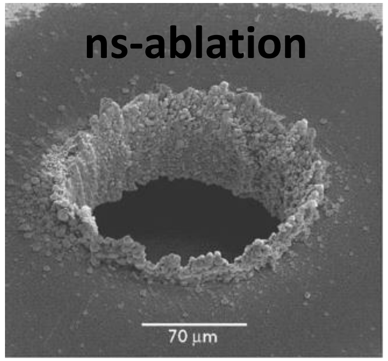


$$\tau_{coll} \approx 10^{-13}\,s \quad \longrightarrow \quad \tau_{laser} \approx 10^{-9}\,s$$
$$\longrightarrow \quad \tau_{laser} \approx 10^{-15}\,s$$

ABSORPTION :
Laser light is absorbed by interaction with electrons

HEATING:
The excited electrons collide with lattice phonons and with other electrons and increase their energy

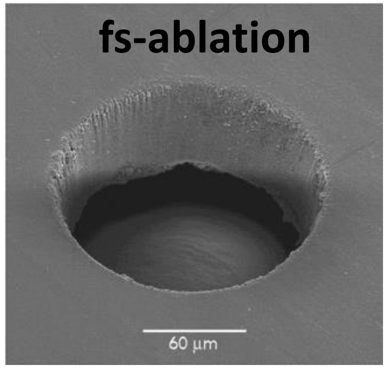
- surface temperature, pressure and charge rapidly increase
- surface explodes (breakdown, coulomb explosion) → **ablation**
  → **stoichiometric process**



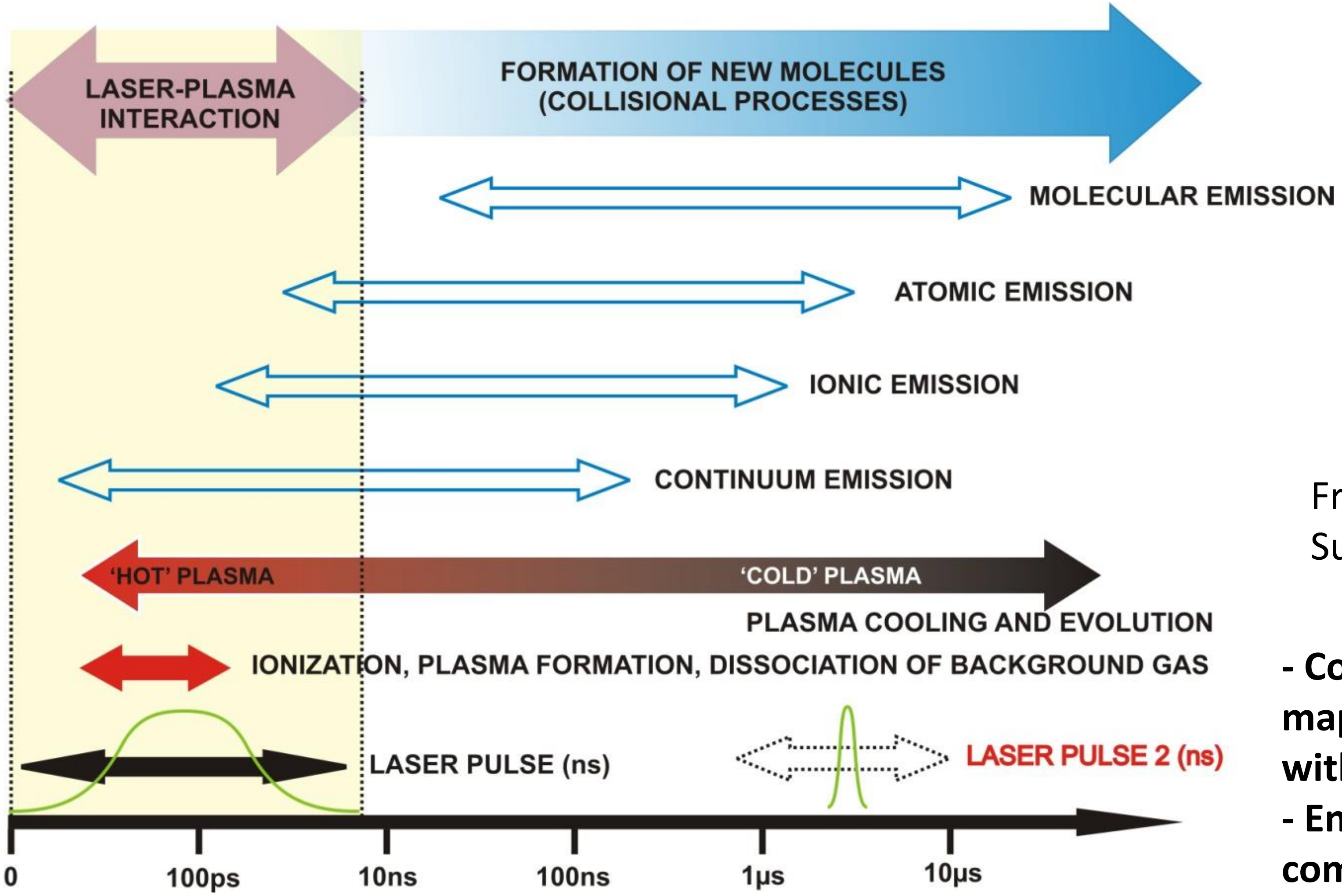
In times of the order of the duration of **ns laser pulse** the electrons will make many collisions

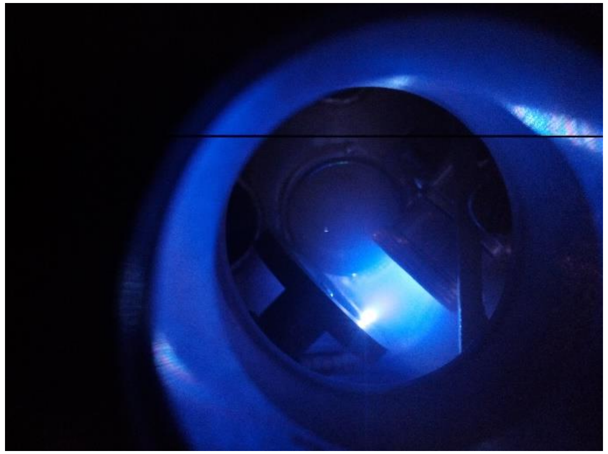
Optical energy is instantaneously turned into heat (heat diffusion)

During **fs laser pulse** electron collisions are rare.
No heat diffusion, no nano and micro droplets



Laser Plasma evolution

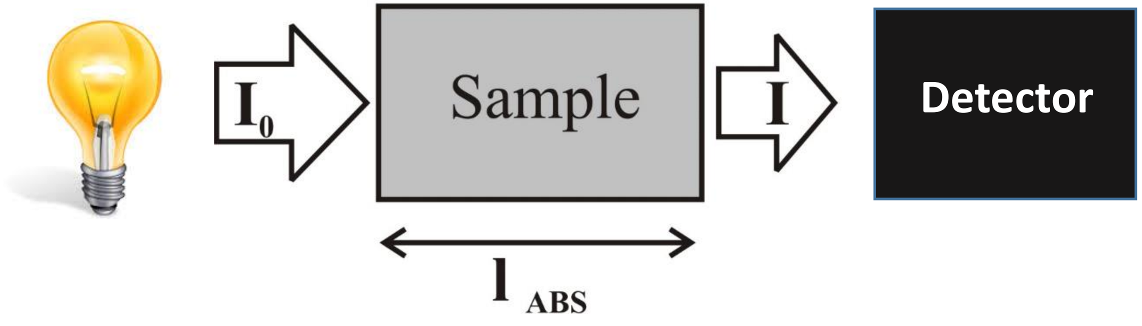




Free expansion in vacuum
Suppressed expansion in gasses

- **Complete temporal and spatial mapping of plasma constituents with Cavity Ring-Down Spectroscopy**
- **Enhanced analysis of target composition**

Classical absorption principle



$$I = I_0 \cdot \exp(-N \cdot \sigma(\lambda) \cdot l_{ABS})$$

- **Intensity ratio (magnitude)**
- Lowest particle number density:

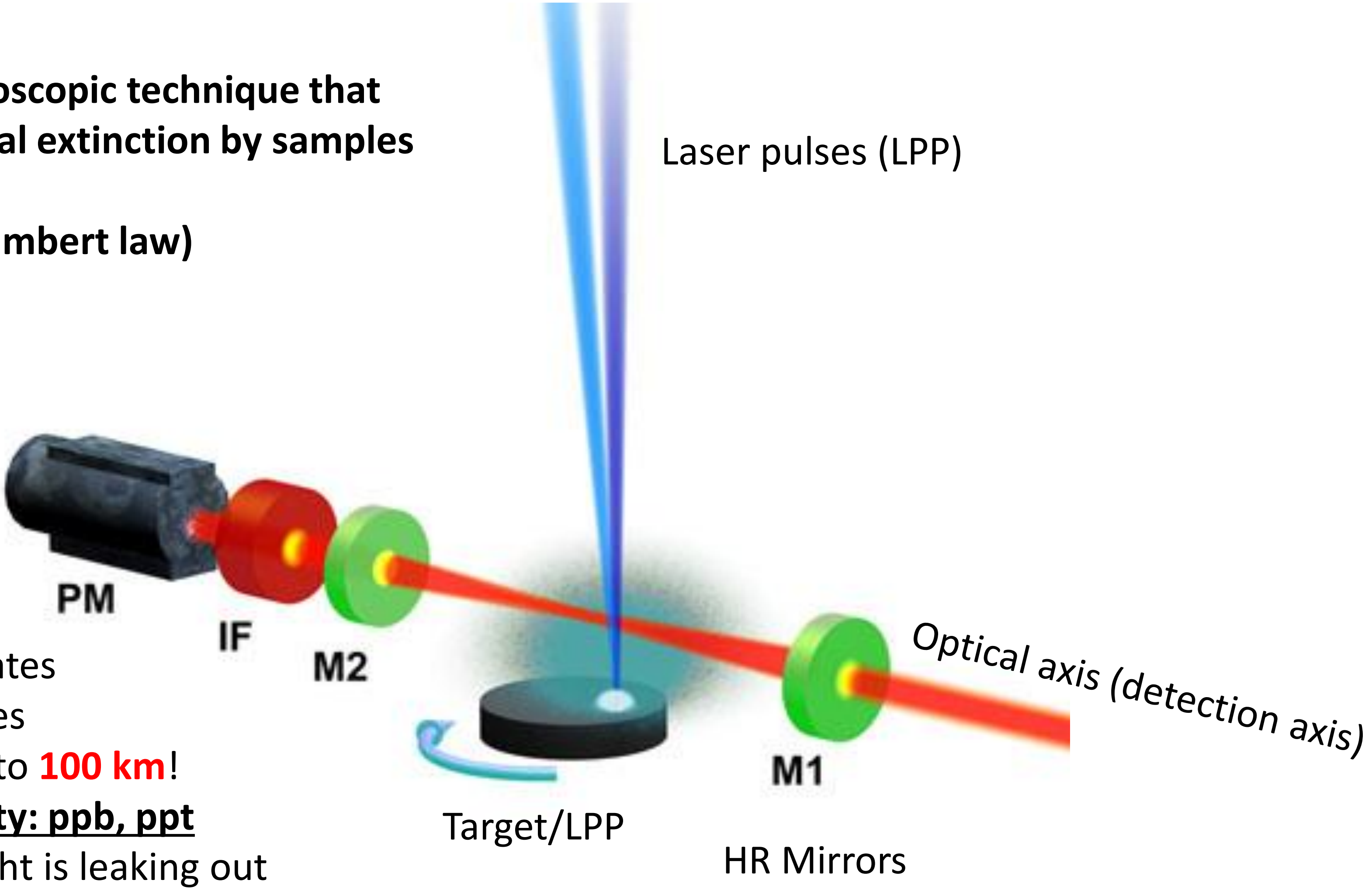
$$N_{min} = \left(\frac{\Delta I}{I_0}\right)_{NOISE} \Big/ \sigma(\lambda) \cdot l_{ABS}$$

- Limiting factor – light source noise
  - stable sources
- Short absorption path-length
  - Multipass cell
- Sensitivity usually up to ppm range

Cavity Ring-Down Spectroscopy principle

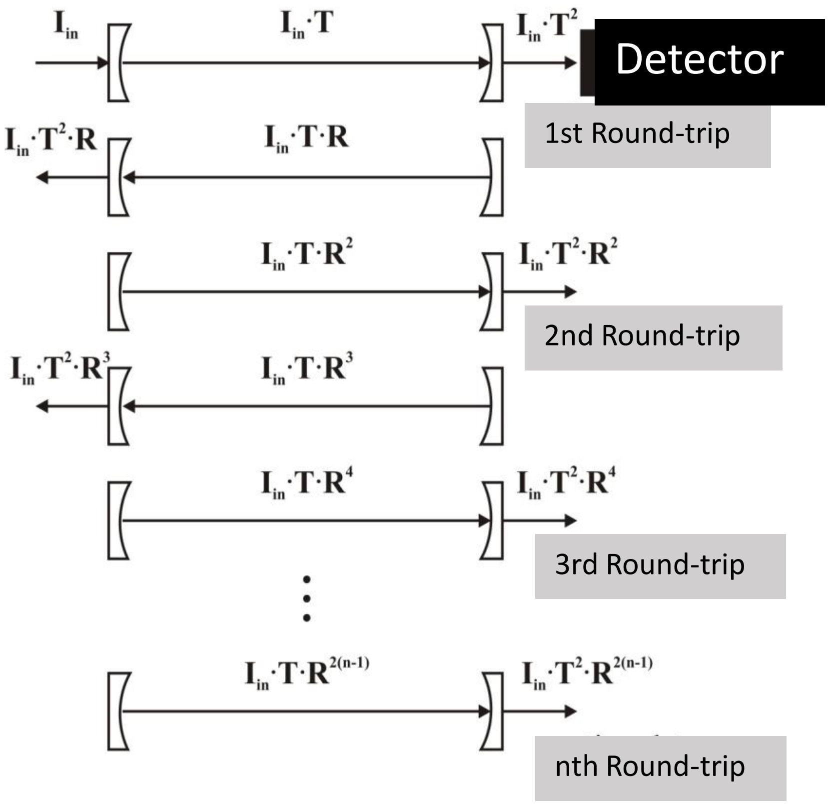
CRDS is a highly sensitive optical spectroscopic technique that enables measurement of absolute optical extinction by samples that scatter and absorb light.

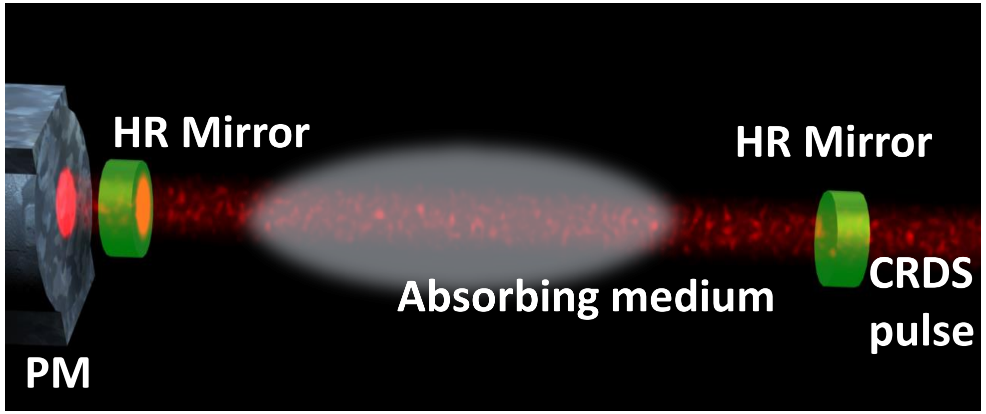
- **Direct absorption technique (Beer-Lambert law)**



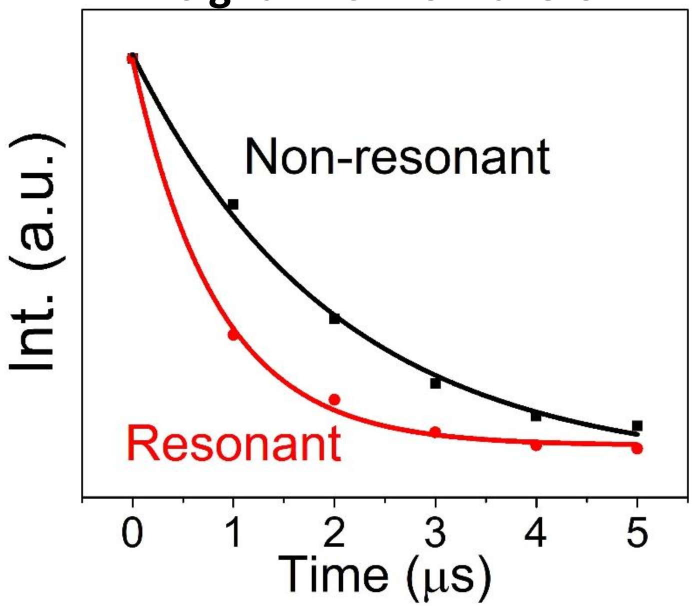
Laser light is coupled into cavity and oscillates back and forth between mirrors many times **increasing** the **absorption path-length** up to **100 km**! (our case 100s of meters) -> **<u>High sensitivity: ppb, ppt</u>**
Upon each reflection a small fraction of light is leaking out (decay time->waveform).

Cavity Ring-Down Spectroscopy principle





PM signal – CRDS waveform



CRDS-time which photons spend in resonator – lifetime

ABSORPTION-shorter lifetime

-> single or multi-exponential decay

->**CRDS is based on measuring time, not intensities**

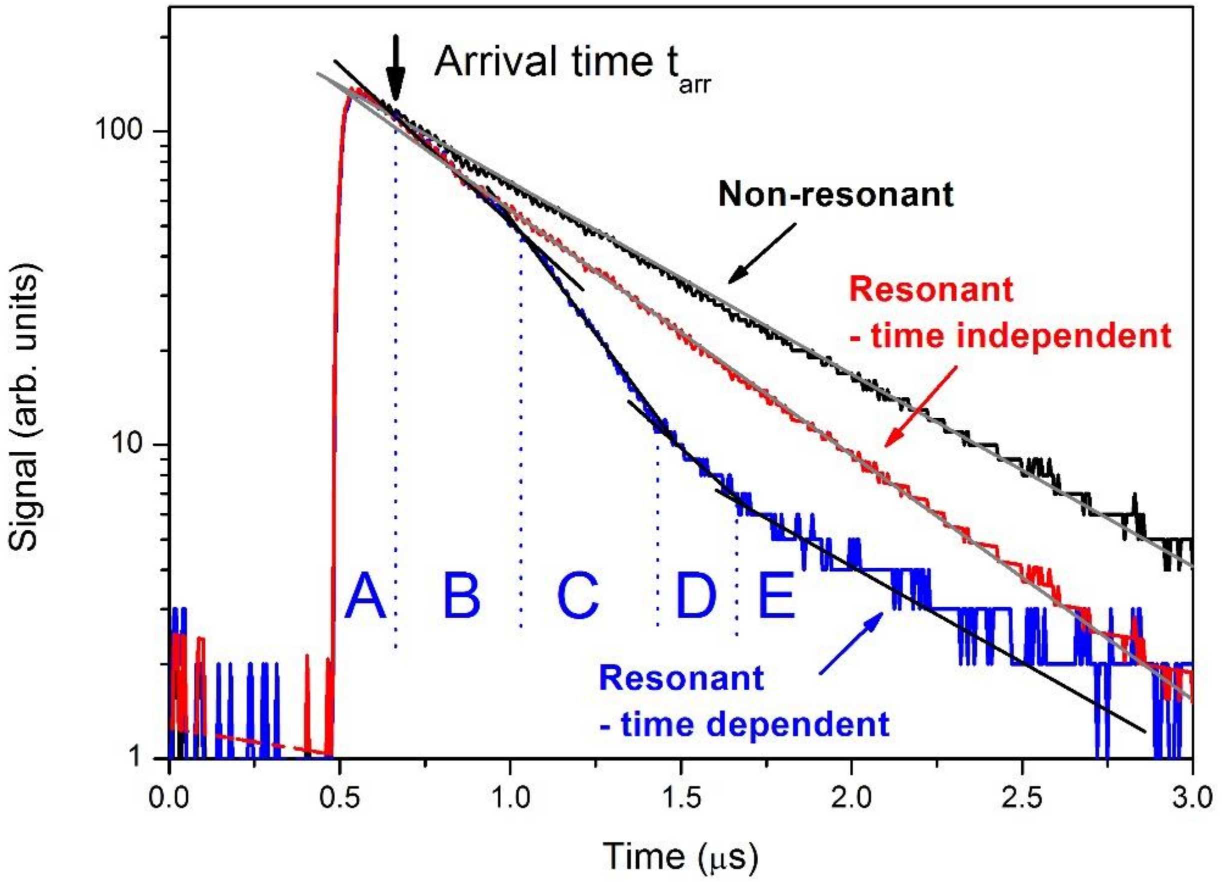
$$I = I_0 \exp(-t/\tau_0)$$

- Limiting factor – mirror reflectivity (R=99.999%)

Cavity Ring-Down Spectroscopy principle

Absorption coeffi
k→k(λ, t)

Time-dependent absorption (semi-log scale)
CRDS waveforms – integration within **time-windows A-E**



- Time independent absorption (within time-windows)

$$k_\lambda = \frac{L}{l \cdot c} \cdot \left(\frac{1}{\tau} - \frac{1}{\tau_0}\right)$$

τ_0 - lifetime empty cavity (or no resonance-no absorption)
τ – lifetime of photons in a case of absorption (resonance)

- Time-dependent absorption

$$k_{\lambda,t} = \frac{L}{l \cdot c}\frac{d}{dt}\left[ln\left(\frac{I(t)}{I_0}\right)\right] - (1-R)/l$$

Absorption coefficient – **cavity loss**
[cm^{-1}]

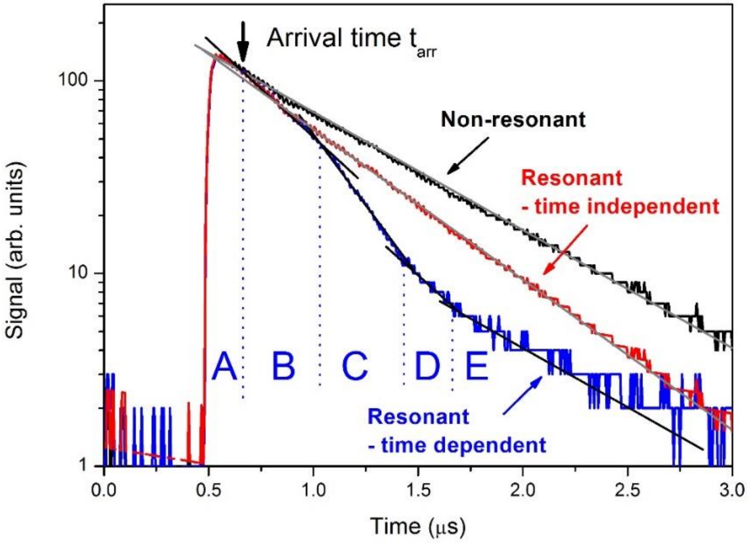
Time-resolved spectrum in absolute units:
k [cm^{-1}] vs. λ [nm]

Allows us to measure concentrations!

Cavity Ring-Down Spectroscopy principle

Dynamics and molecular formation of LPP

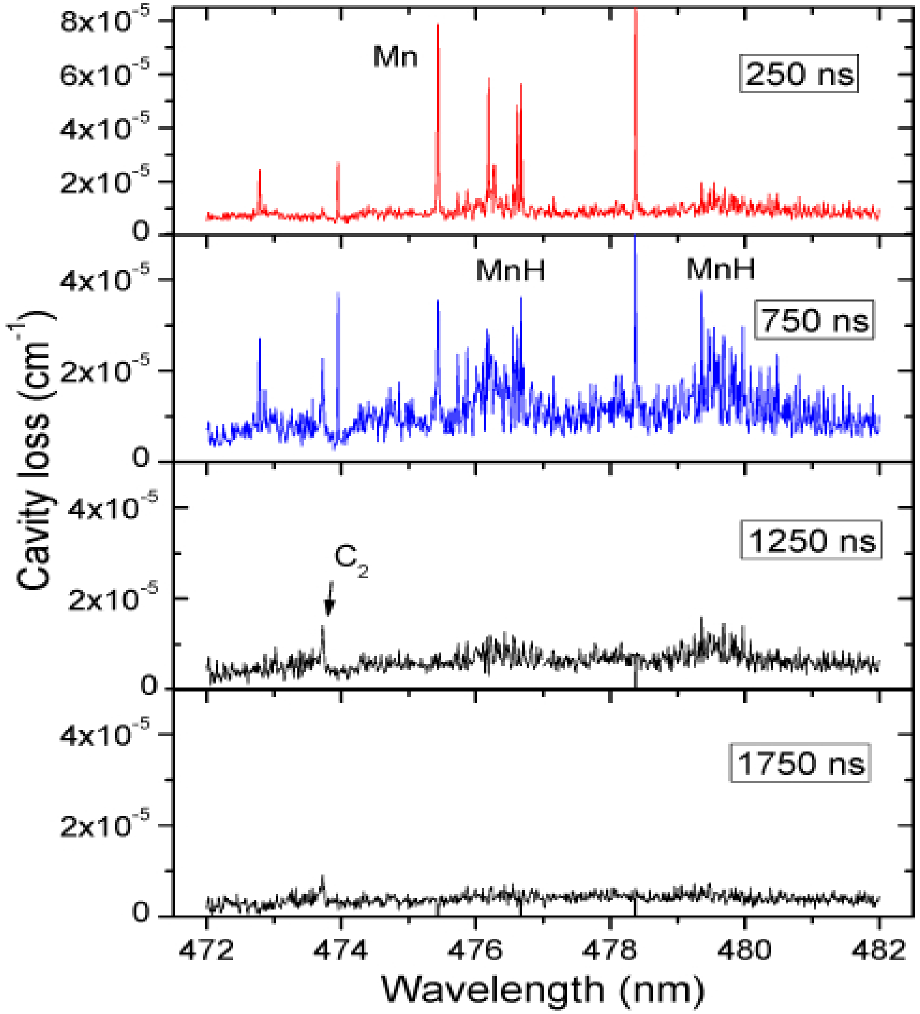
CRDS waveforms (semi-log scale)



Evaluation of
waveform
within
time-windows

Dynamics of LPP
(temporal evolution)

TOF CRDS

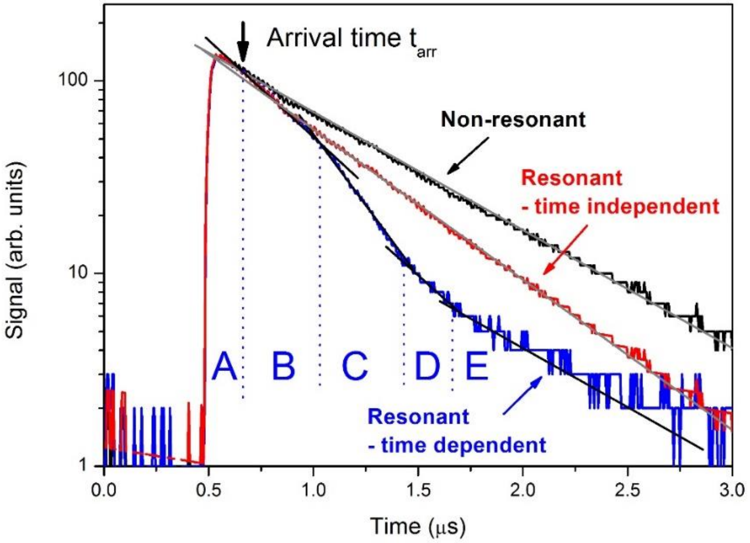


N. Krstulović et al, Eur Phys J D **37** (2006) 209-15

Cavity Ring-Down Spectroscopy principle

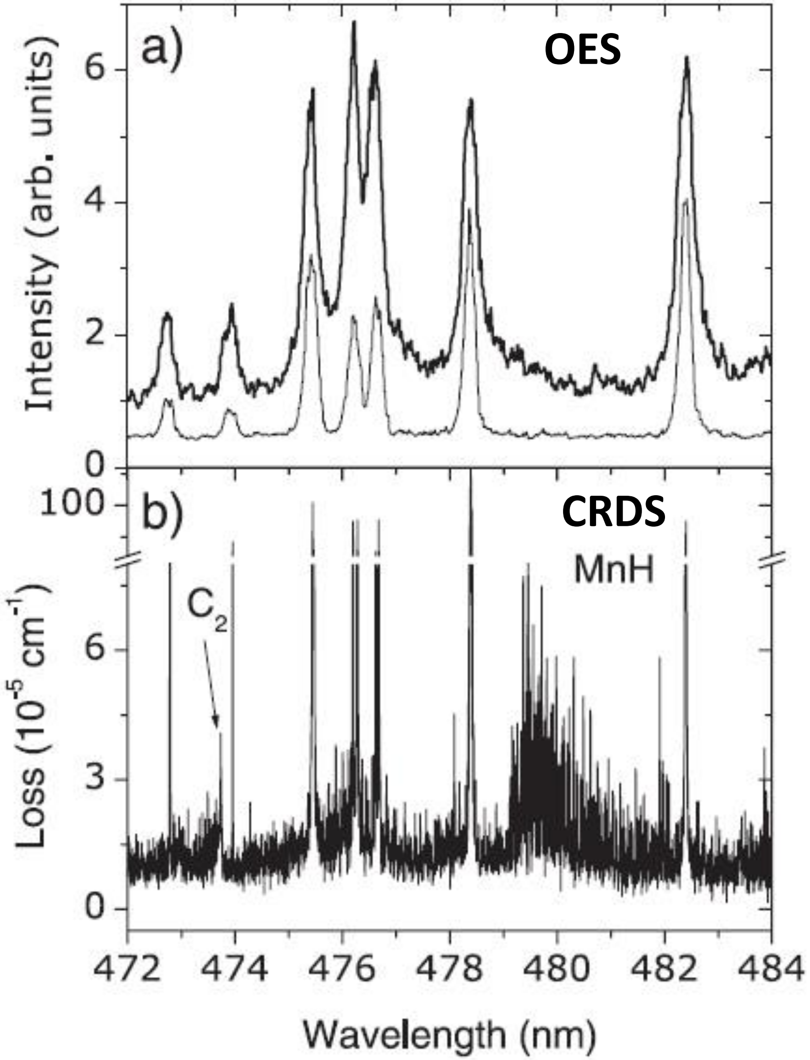
Dynamics and molecular formation of LPP

CRDS waveforms (semi-log scale)



Evaluation of
waveform
within
time-windows

Emission (OES, LIBS) vs.
Absorption (CRDS)

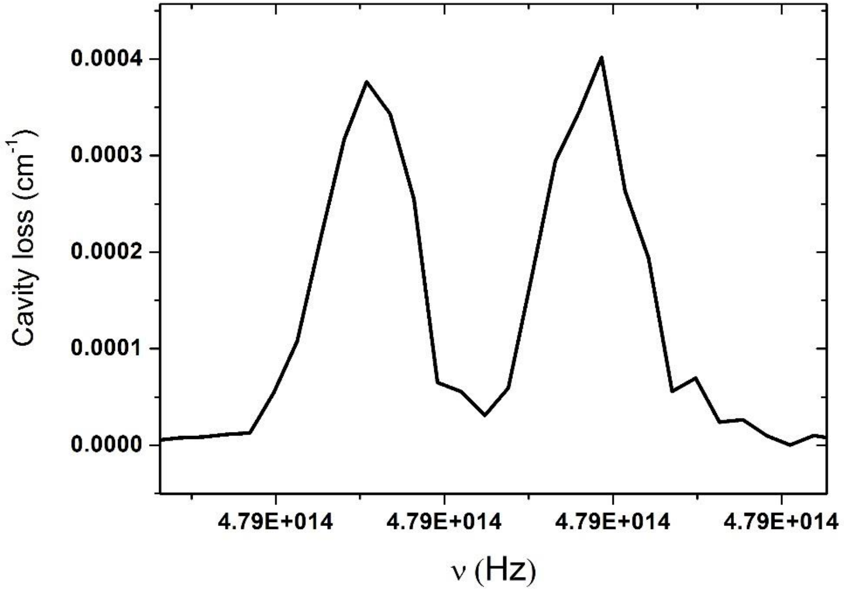


N. Krstulović et al, Eur Phys J D **37** (2006) 209-15

Cavity Ring-Down Spectroscopy principle

Concentration determinations

CRDS spectrum in frequency domain

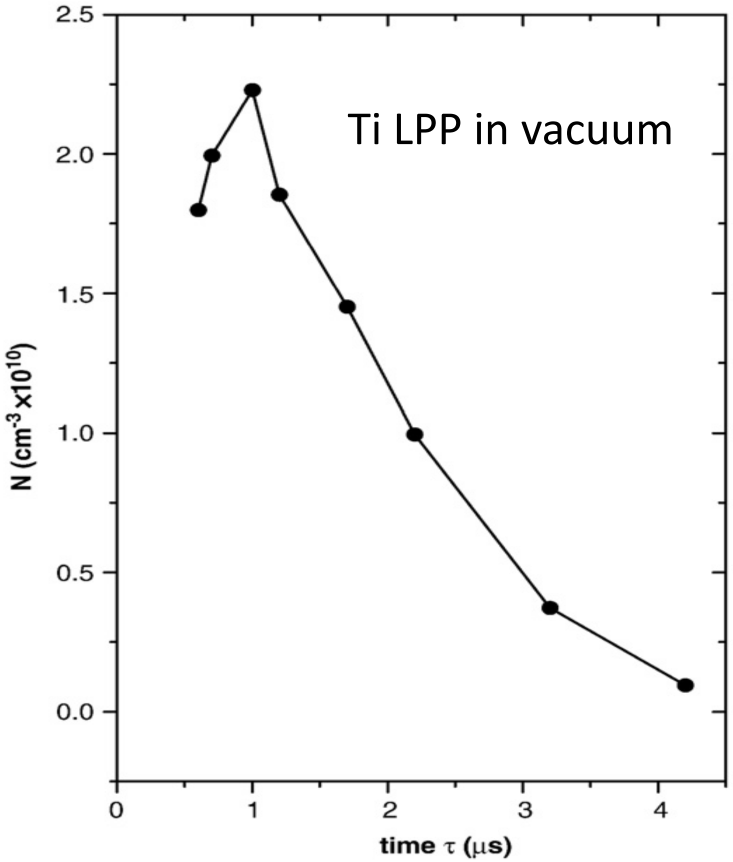


$$k_\lambda = \frac{L}{l \cdot c} \cdot \left(\frac{1}{\tau} - \frac{1}{\tau_0}\right)$$

$$\int k_\nu \cdot d\nu = \frac{\lambda_0}{8\Pi} \cdot \frac{g_2}{g_1} \cdot \frac{N}{\tau_{up}}$$

N – number density [cm^{-3}]

Concentration of LPP species:

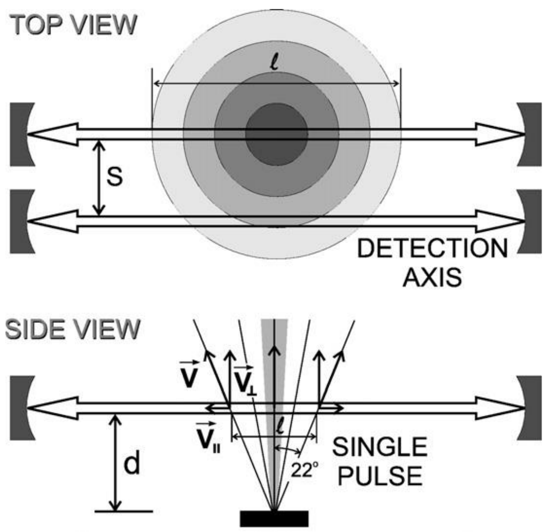


The integral of the measured absorption coefficient k_ν in frequency domain is proportional to the number density of absorbing atoms N.

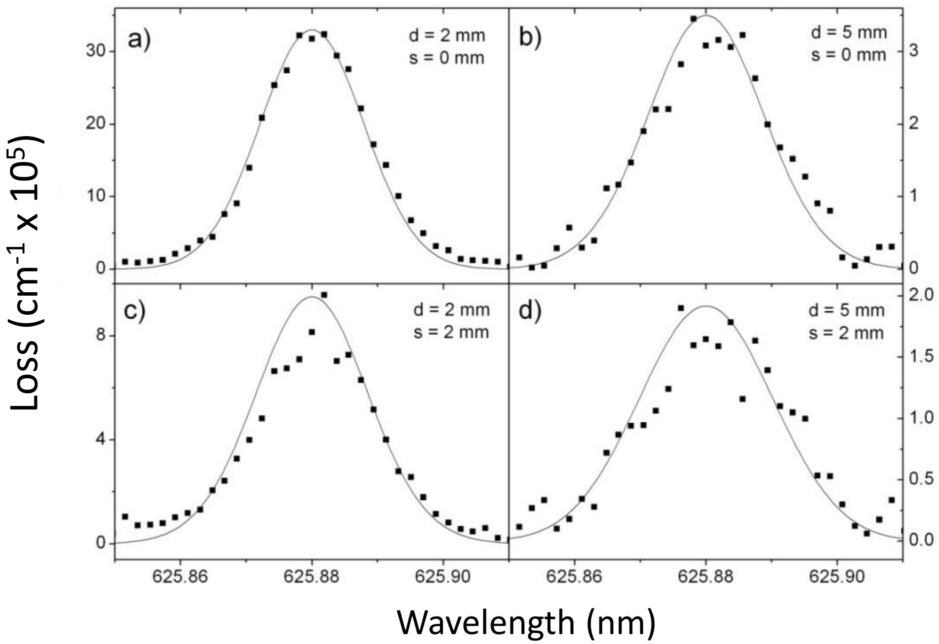
λ_0 is a wavelength at the center of the line, g_1 and g_2 are statistical weights of the lower and upper level, respectively, τ_{up} is a lifetime of an atom in the upper level.

Cavity Ring-Down Spectroscopy principle

Concentration determinations



Ti LPP in vacuum



2D mapping of the plasma plume
\+
Plume axially symmetric
\+
Evaluation within Time-windows
=
Temporally resolved 3D mapping of all species in plasma plume

d – orthogonal distance
s – lateral distance

d = 2 mm s = 0 mm	d = 5 mm s = 0 mm	d = 2 mm s = 2 mm	d = 5 mm s = 2 mm
$4.7 \cdot 10^8$ cm^{-3}	$5.6 \cdot 10^7$ cm^{-3}	$1.5 \cdot 10^8$ cm^{-3}	$3.5 \cdot 10^7$ cm^{-3}

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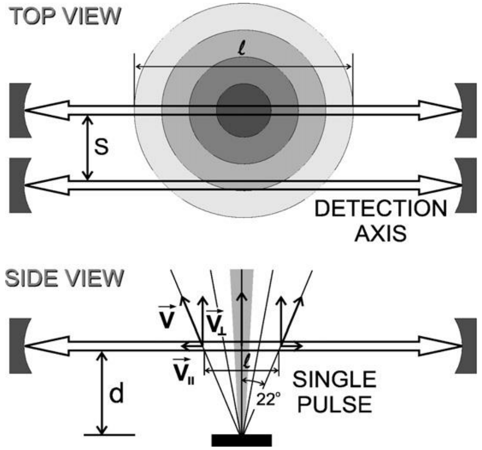
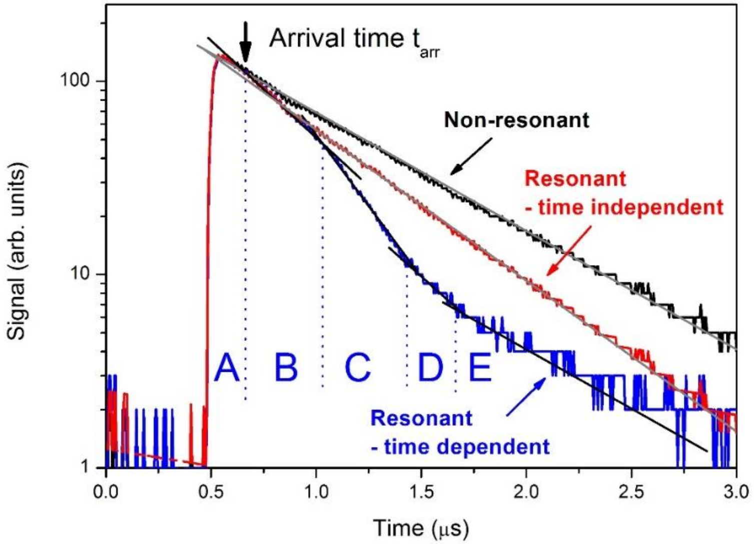
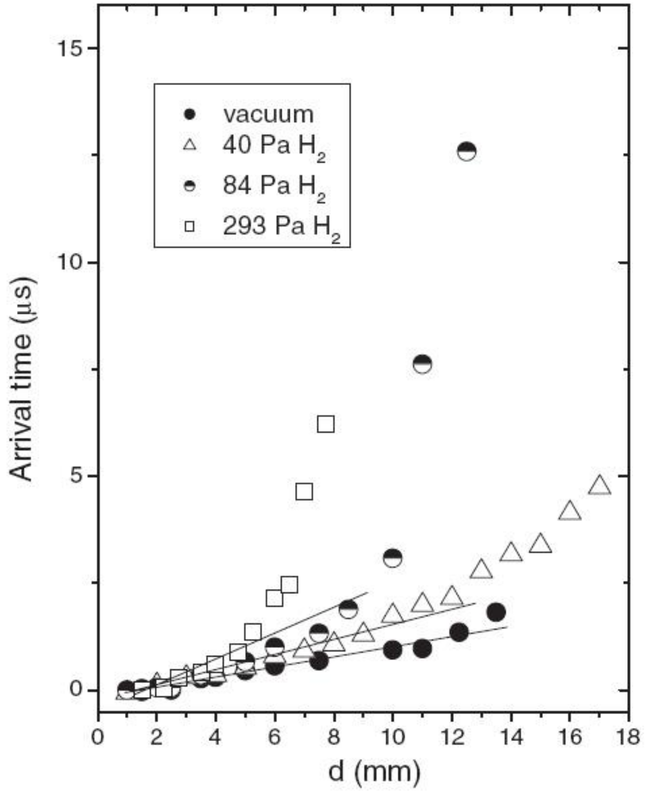
Velocity determination by CRDS



Velocity – arrival time vs. distance
(between cavity axis and target surface)



LPP of Graphite – C2

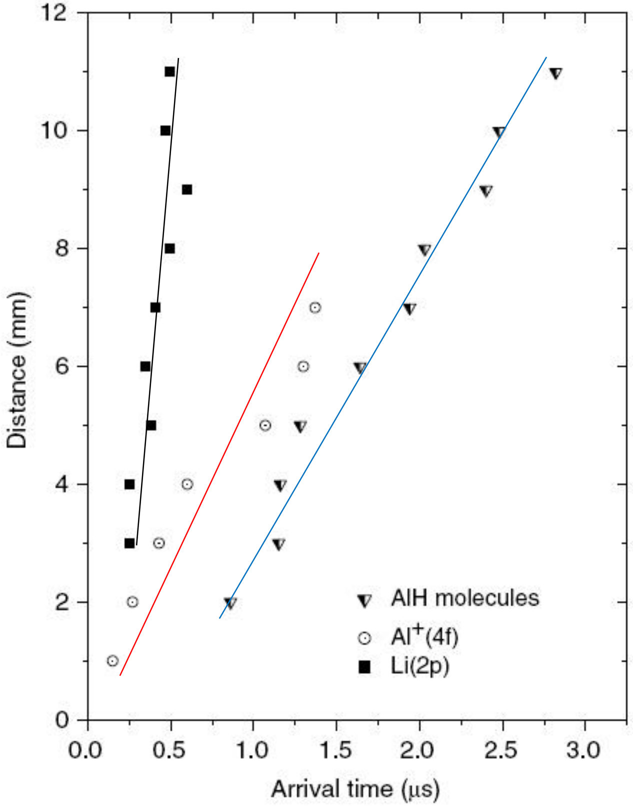


Drag-force model

$$d = d_0 \cdot (1 - \exp(-bt))$$

b – de-acceleration factor

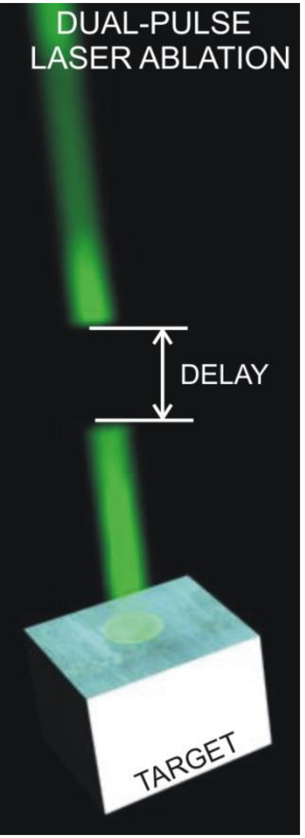
LPP of $LiAlH_4$

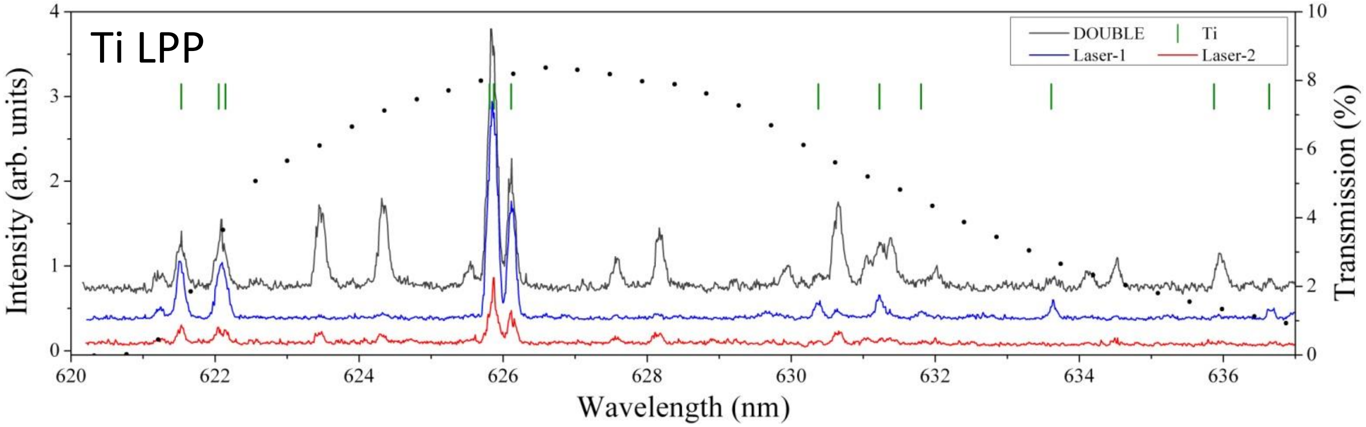


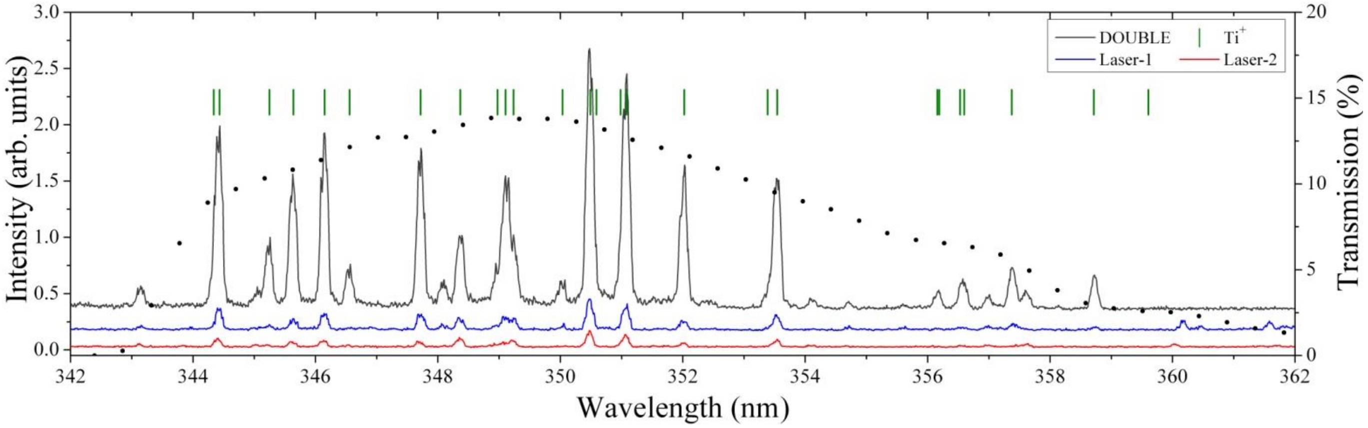
Free expansion in vacuum

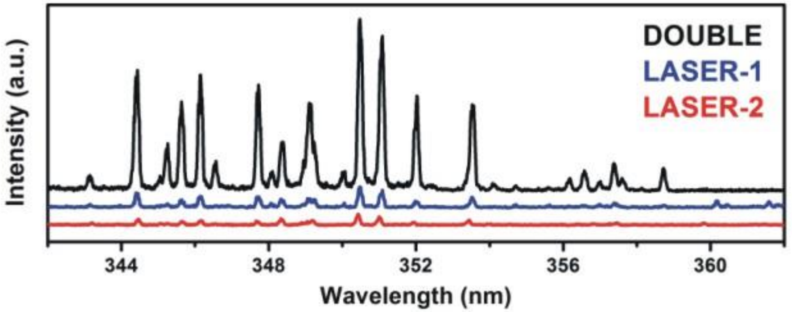
Labazan et al, Chemical Physics Letters 428 (2006) 13–17

Double pulse laser ablation (DPLA)





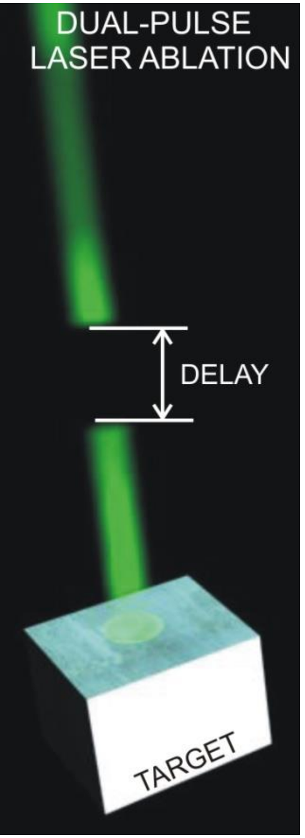


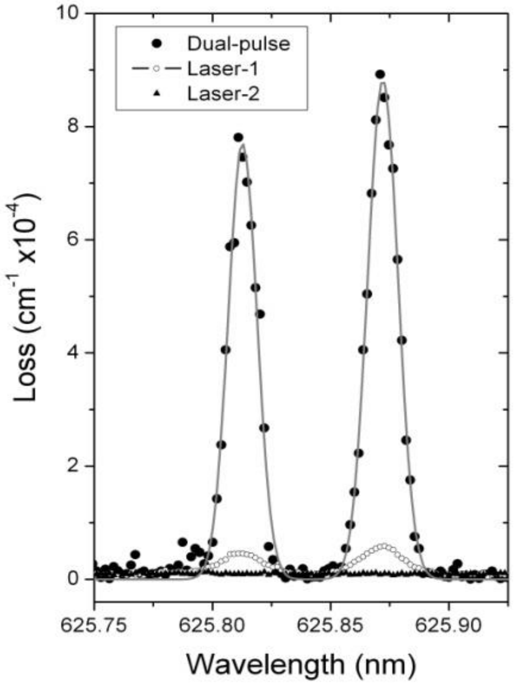


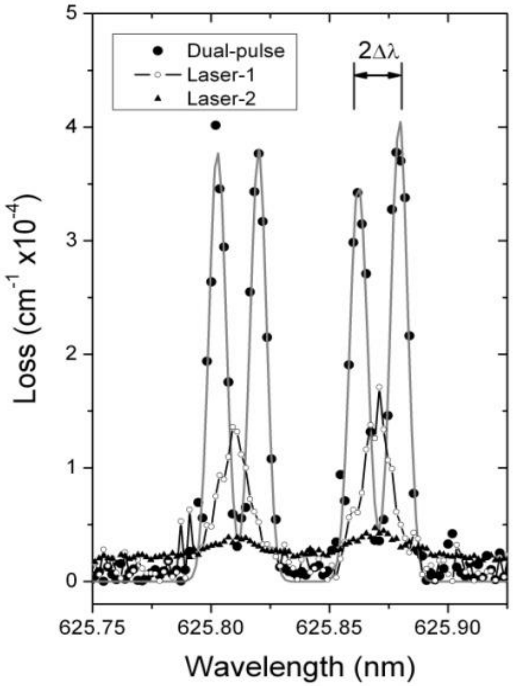
Eur. Phys. J. D (2015) 69: 98
SAB 107 (2015) 67–74

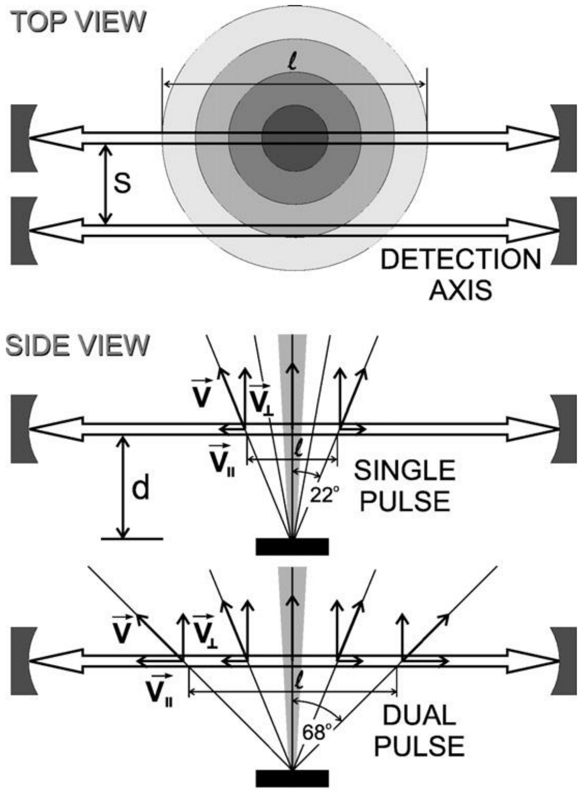
DPLA – significant improvement of analytical capabilities –
better stoichiometry and better sensitivity (trace particles detection)

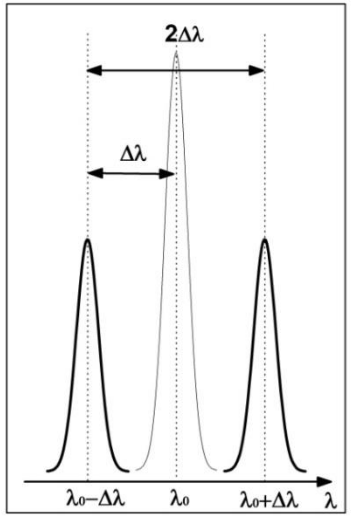
Double pulse laser ablation











Ablation angle increased

Line splitting – lateral velocity component significant

$$\frac{\Delta\lambda}{\lambda} = \frac{|v_{parallel}|}{c}$$

Plasma plume shape delicate

N. Krstulovic et. al, *SAB* 64 (2009)

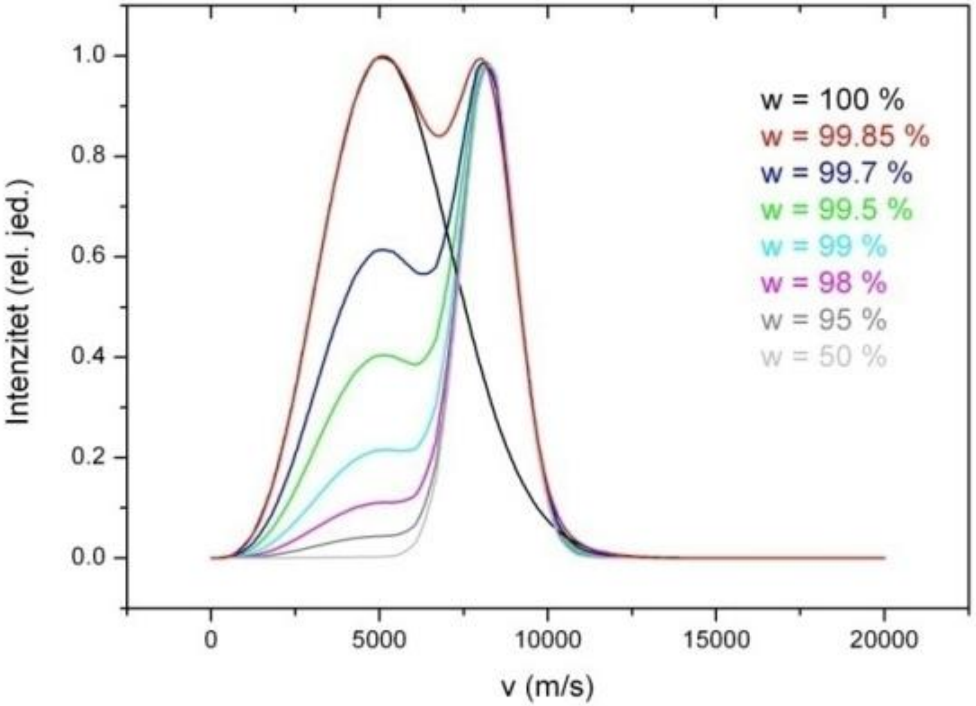
Cavity Ring-Down Spectroscopy principle

Profile of absorption spectral line:

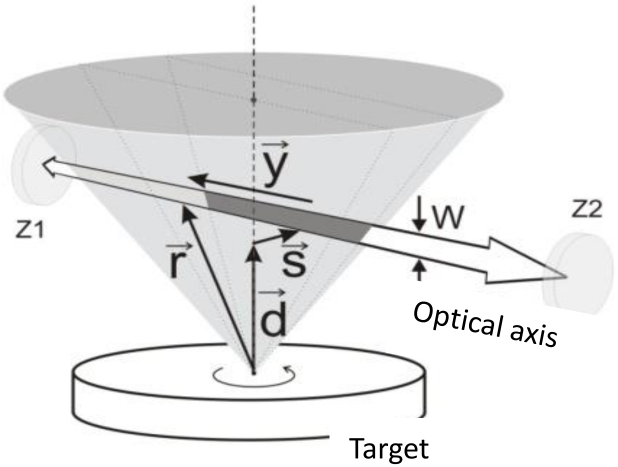
$$S(v) = \iint N(v) \cdot m(v, w, r(y), T, \Delta T) \cdot g(y, s, d) \cdot [\delta(v - v_0 - \Delta v) + \delta(v - v_0 + \Delta v)] \cdot dv \cdot dy$$

Maxwell-Boltzmann
velocity distribution

- Bimodal
(Fast and slow peak)



CRDS geometry



Cavity Ring-Down Spectroscopy principle

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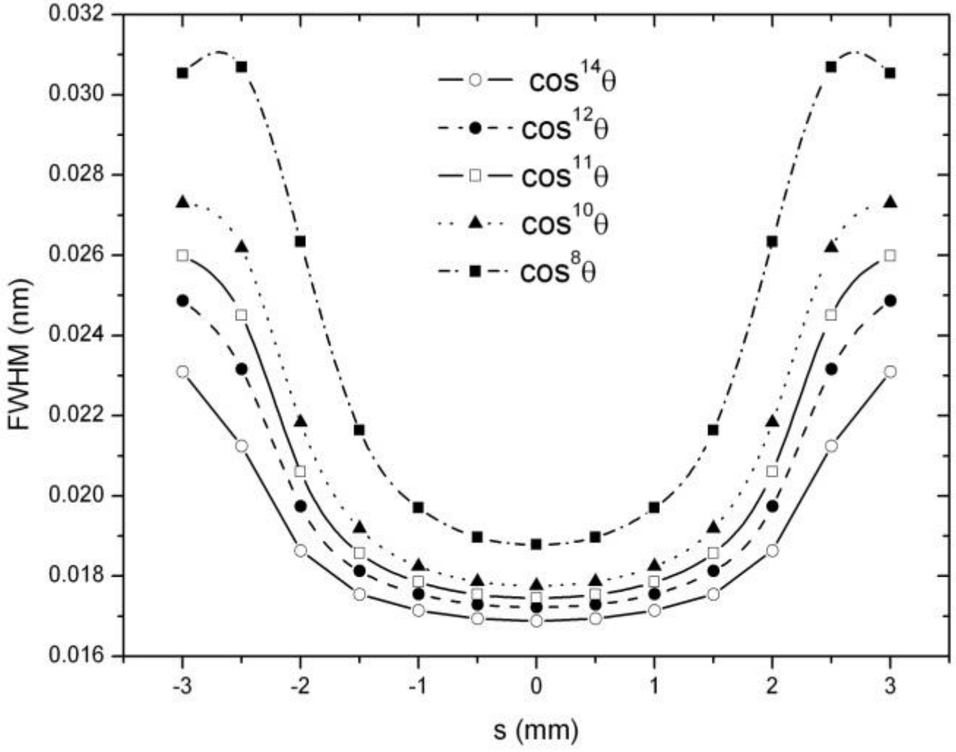
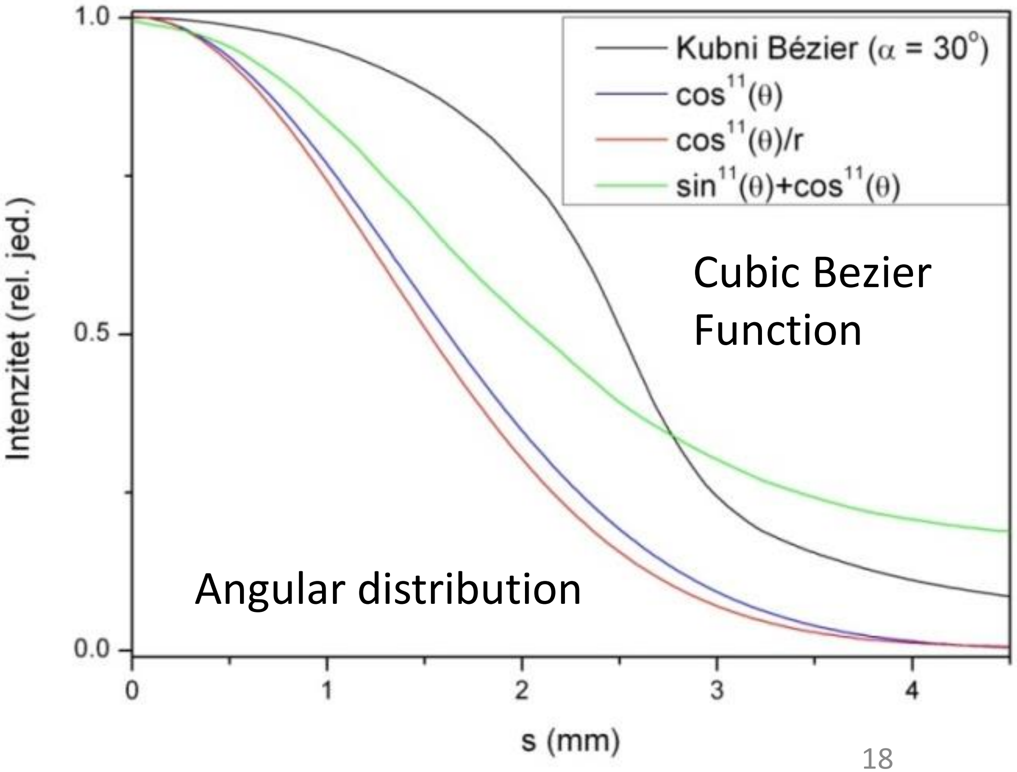
FWHM



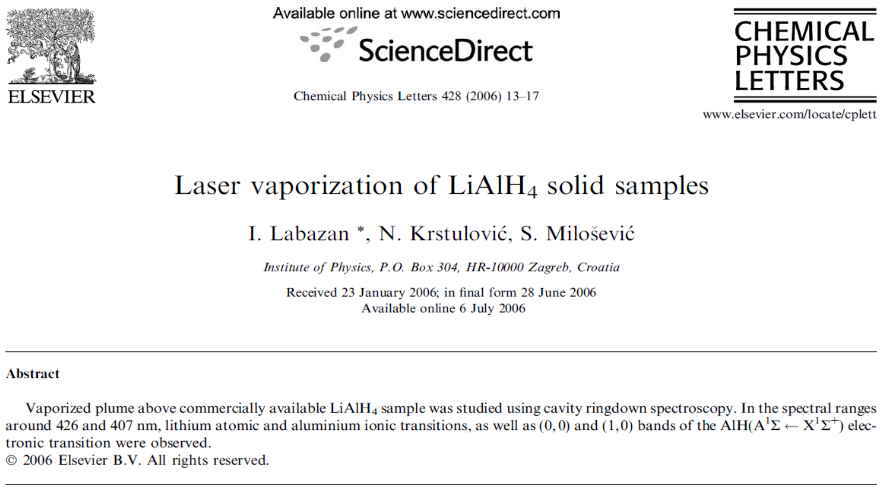


Cubic Bezier Function

Angular distribution

CRDS detection of Li from LPP

Time resolved spectra of laser produced plasma of LiAlH target



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Laser vaporization of $LiAlH_4$ solid samples

I. Labazan *, N. Krstulović, S. Milošević

Institute of Physics, P.O. Box 304, HR-10000 Zagreb, Croatia

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Abstract

Vaporized plume above commercially available $LiAlH_4$ sample was studied using cavity ringdown spectroscopy. In the spectral ranges around 426 and 407 nm, lithium atomic and aluminium ionic transitions, as well as (0,0) and (1,0) bands of the $AlH(A^1\Sigma \leftarrow X^1\Sigma^+)$ electronic transition were observed.

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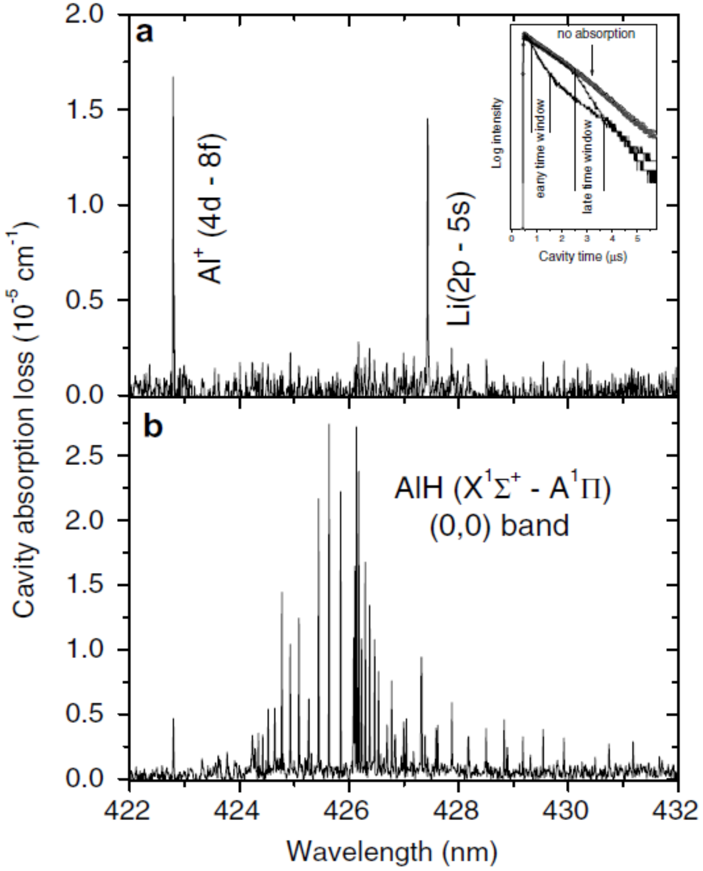
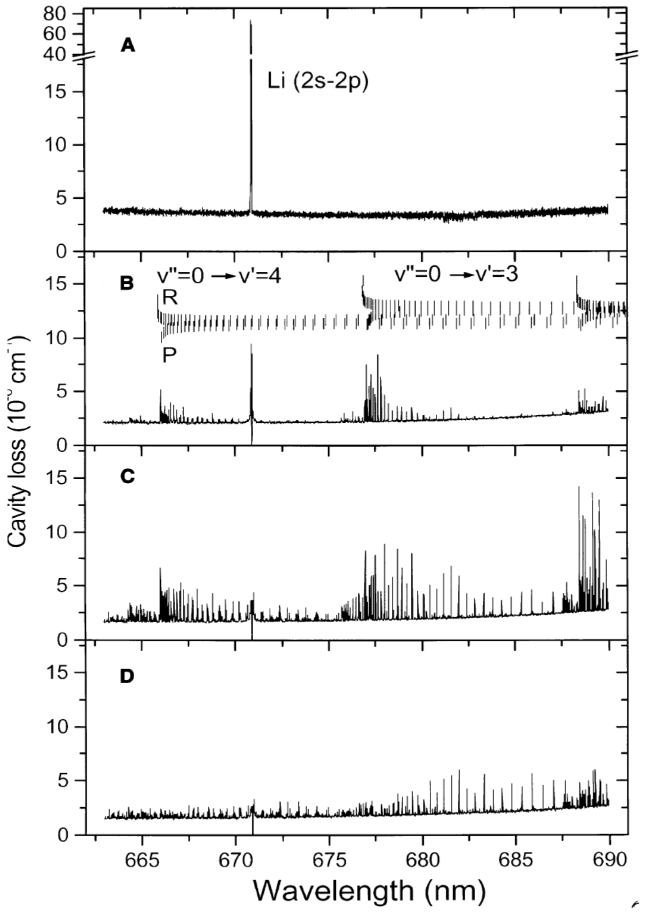
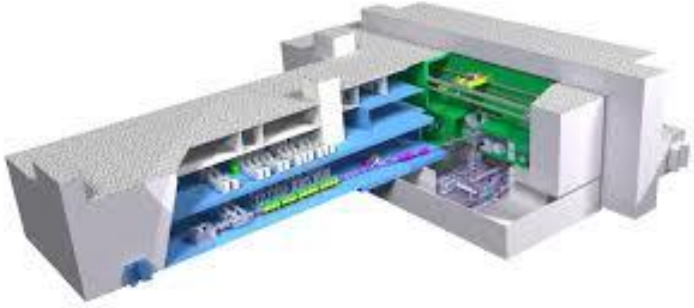




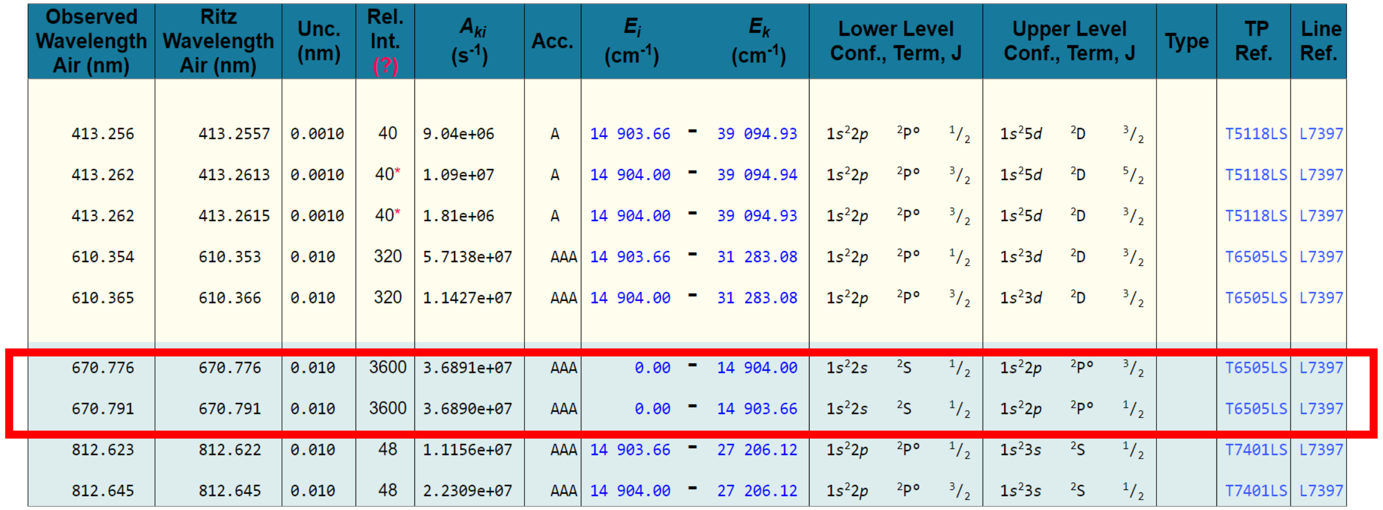
CRDS determination od monitoring of Li from laser plasmas based on Li 2p-5s line.
Determination of velocity of ablated Li atoms by CRDS.
Mapping of laser plasma and Li atoms in time and space – full space determination of Li evolution in laser plasmas.

CRDS detection of Li, D, T and Be @ DONES (Granada, Spain)



Cavity Ring-Down Spectroscopy

- **cross-check for others diagnostics techniques (ne, Te, T and n of species)**
- **Analysis of exhaust gasses (residuel gasses, detection and quantification) – Li, D, T, Be**

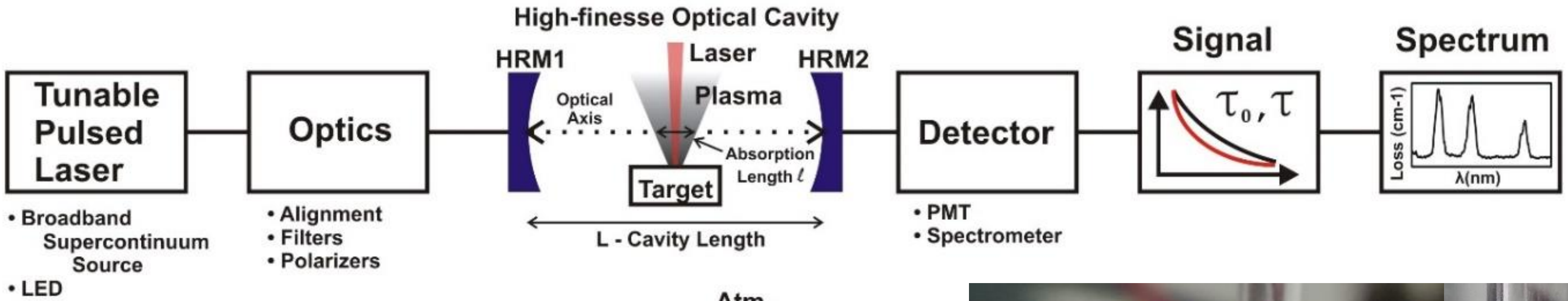


Observed Wavelength Air (nm)	Ritz Wavelength Air (nm)	Unc. (nm)	Rel. Int. (?)	A_{ki} (s^{-1})	Acc.	E_i (cm^{-1})		E_k (cm^{-1})	Lower Level Conf., Term, J			Upper Level Conf., Term, J			Type	TP Ref.	Line Ref.
413.256	413.2557	0.0010	40	9.04e+06	A	14 903.66	-	39 094.93	$1s^22p$	$^2P^\circ$	$^1/_2$	$1s^25d$	^2D	$^3/_2$		T5118LS	L7397
413.262	413.2613	0.0010	40*	1.09e+07	A	14 904.00	-	39 094.94	$1s^22p$	$^2P^\circ$	$^3/_2$	$1s^25d$	^2D	$^5/_2$		T5118LS	L7397
413.262	413.2615	0.0010	40*	1.81e+06	A	14 904.00	-	39 094.93	$1s^22p$	$^2P^\circ$	$^3/_2$	$1s^25d$	^2D	$^3/_2$		T5118LS	L7397
610.354	610.353	0.010	320	5.7138e+07	AAA	14 903.66	-	31 283.08	$1s^22p$	$^2P^\circ$	$^1/_2$	$1s^23d$	^2D	$^3/_2$		T6505LS	L7397
610.365	610.366	0.010	320	1.1427e+07	AAA	14 904.00	-	31 283.08	$1s^22p$	$^2P^\circ$	$^3/_2$	$1s^23d$	^2D	$^3/_2$		T6505LS	L7397
670.776	670.776	0.010	3600	3.6891e+07	AAA	0.00	-	14 904.00	$1s^22s$	^2S	$^1/_2$	$1s^22p$	$^2P^\circ$	$^3/_2$		T6505LS	L7397
670.791	670.791	0.010	3600	3.6890e+07	AAA	0.00	-	14 903.66	$1s^22s$	^2S	$^1/_2$	$1s^22p$	$^2P^\circ$	$^1/_2$		T6505LS	L7397
812.623	812.622	0.010	48	1.1156e+07	AAA	14 903.66	-	27 206.12	$1s^22p$	$^2P^\circ$	$^1/_2$	$1s^23s$	^2S	$^1/_2$		T7401LS	L7397
812.645	812.645	0.010	48	2.2309e+07	AAA	14 904.00	-	27 206.12	$1s^22p$	$^2P^\circ$	$^3/_2$	$1s^23s$	^2S	$^1/_2$		T7401LS	L7397

Resonant transition

NIST database; Resonsnt transition Li (2s -> 2p)

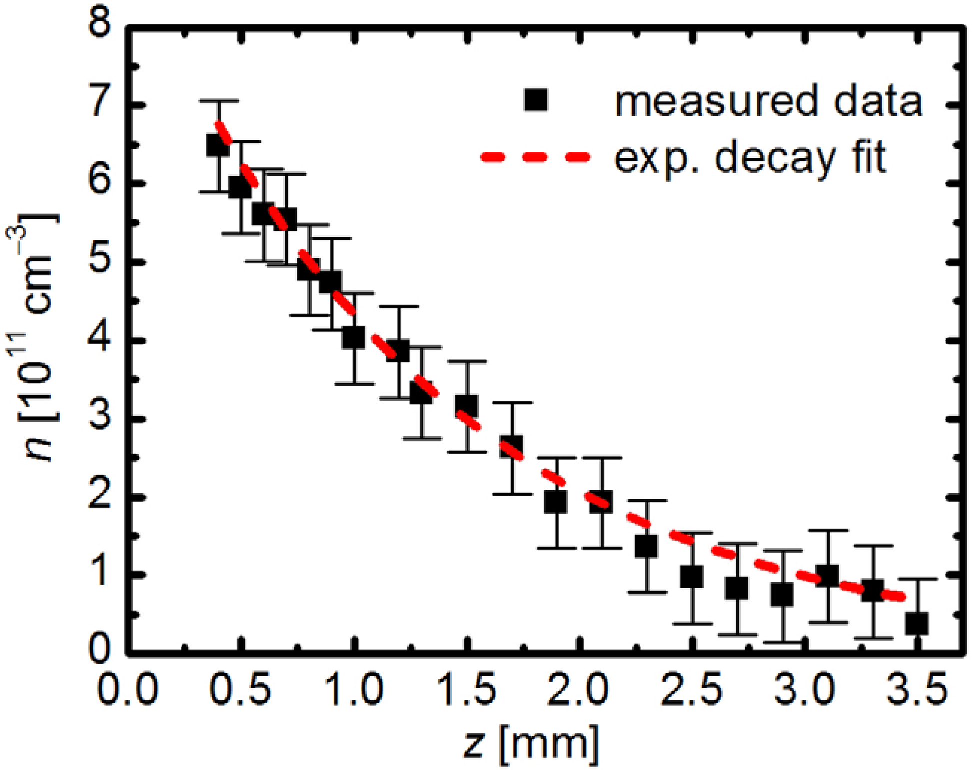
CRDS of Atmspheric Pressure Plasma Jet of Helium

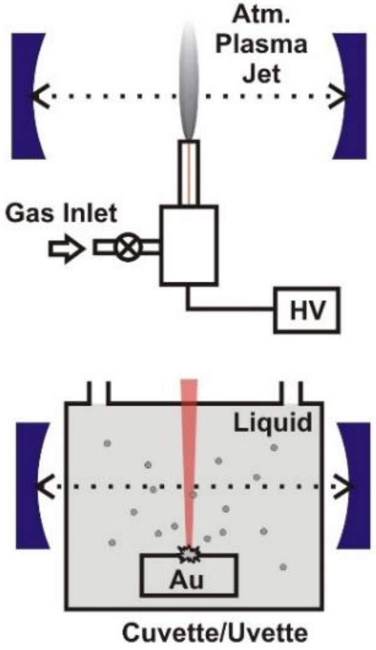


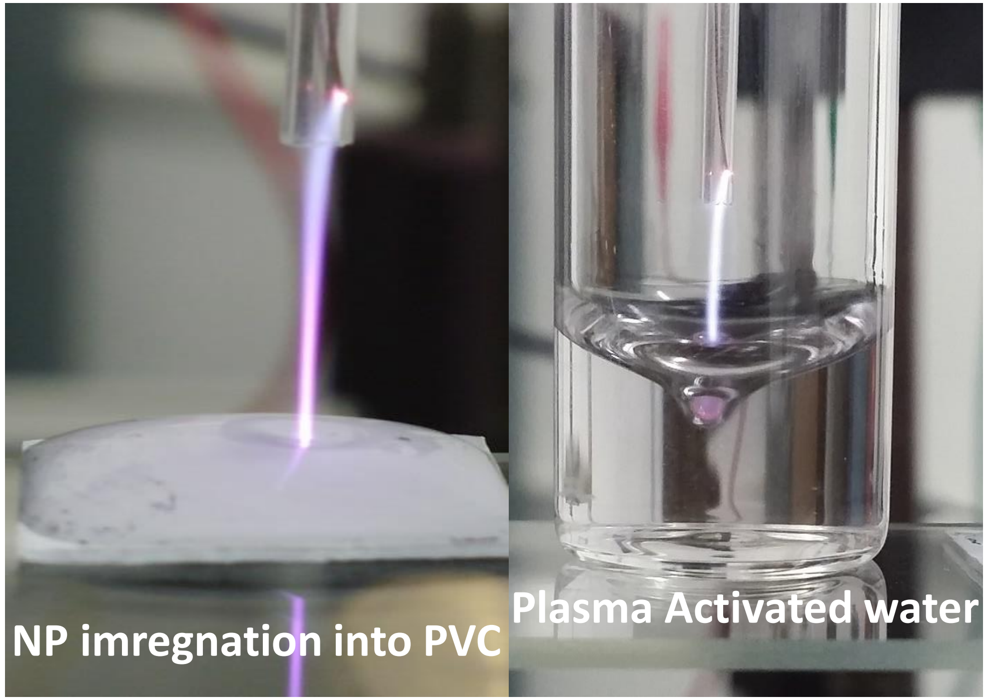
- Broadband Supercontinuum Source
- LED

- Alignment
- Filters
- Polarizers

- PMT
- Spectrometer







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The distribution of He($^3S_1$) metastables along the APPJ

Conclusion

- CRDS - versatile technique to study LPP:
  - Diagnostics / analysis / processes
  - High sensitivity technique (up to ppb and ppt)
    - Low concentration or low probabilities transition detection,
    trace elements, atoms in forbidden states, elements in ground state
  - Velocity determination and dynamics of LPP (time-of-flight selection, Doppler broadening/splitting, model/MB distribution)
    - spatial and temporal evolution of particular species
  - Directly number densities
  - (3+1)D mapping
  - Temperature (Boltzmann, Saha-Boltzmann, Ro-Vib) and electron density (Stark broadening and shift) measurements
  - Complementary to other analytical techniques (e.g. LIBS, OES, TOF-MS)

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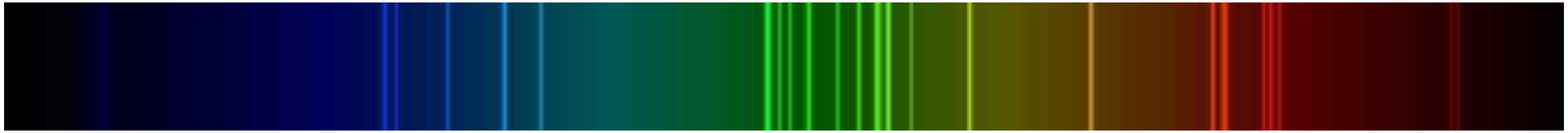
Sulphur (16 electrons)

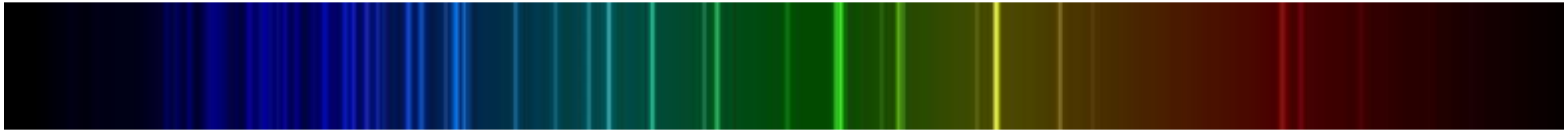


Argon (18 electrons)

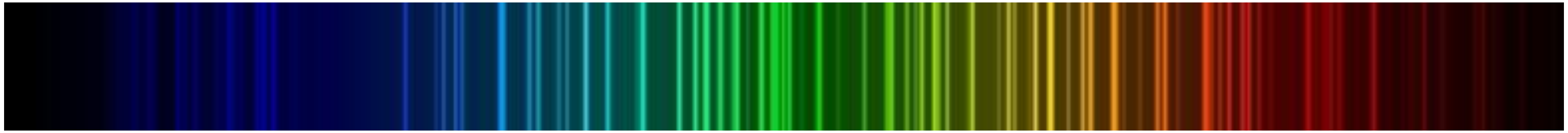
Iron (26 electrons)

Thank you for your attention!

Krypton (36 electrons)



Xenon (54 electrons)



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