CNR IFN
Istituto di Fotonica e Nanotecnologie

POLITECNICO MILANO 1863

FRONTIERS OF ULTRAFAST X-RAY SPECTROSCOPY

CATERINA VOZZI

INSTITUTE FOR PHOTONICS AND NANOTECHNOLOGIES

NATIONAL RESEARCH COUNCIL OF ITALY

UDynI

OSA Short Wavelength Sources and Attosecond/High Field Physics Technical Group

CNR-IFN IN A NUTSHELL

IFN MILANO

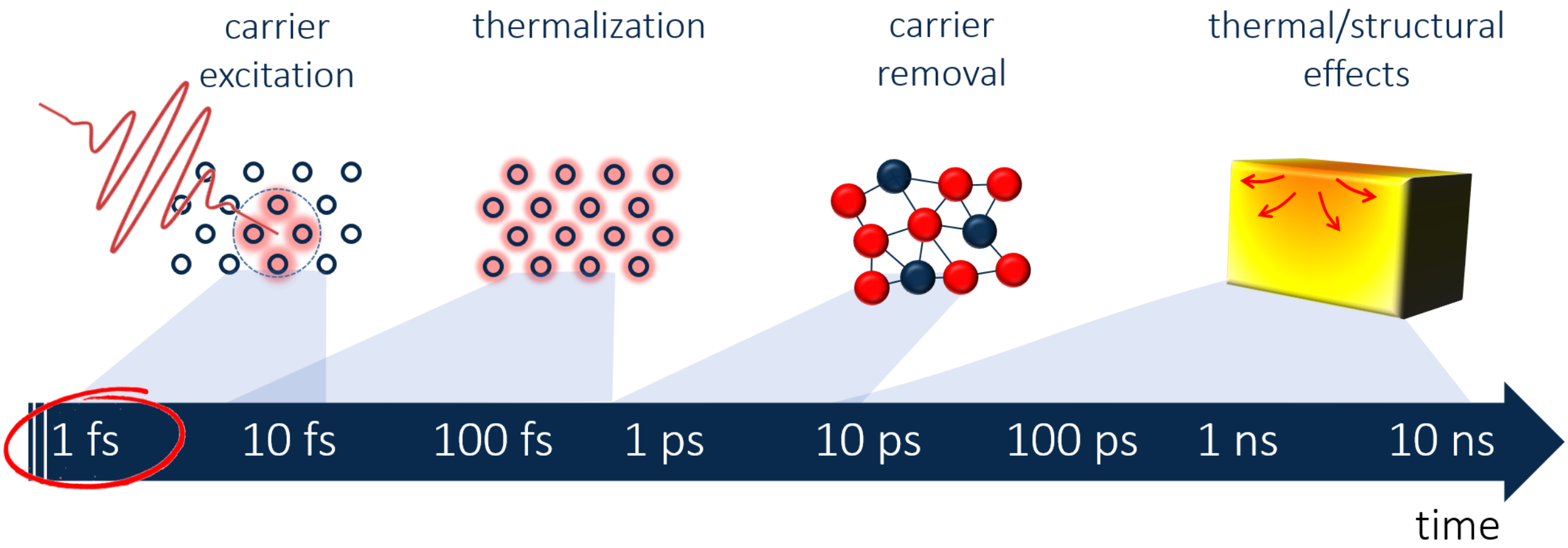
ULTRAFAST DYNAMICS IN MATTER – ATTOSECOND SCIENCE

IFN PADUA

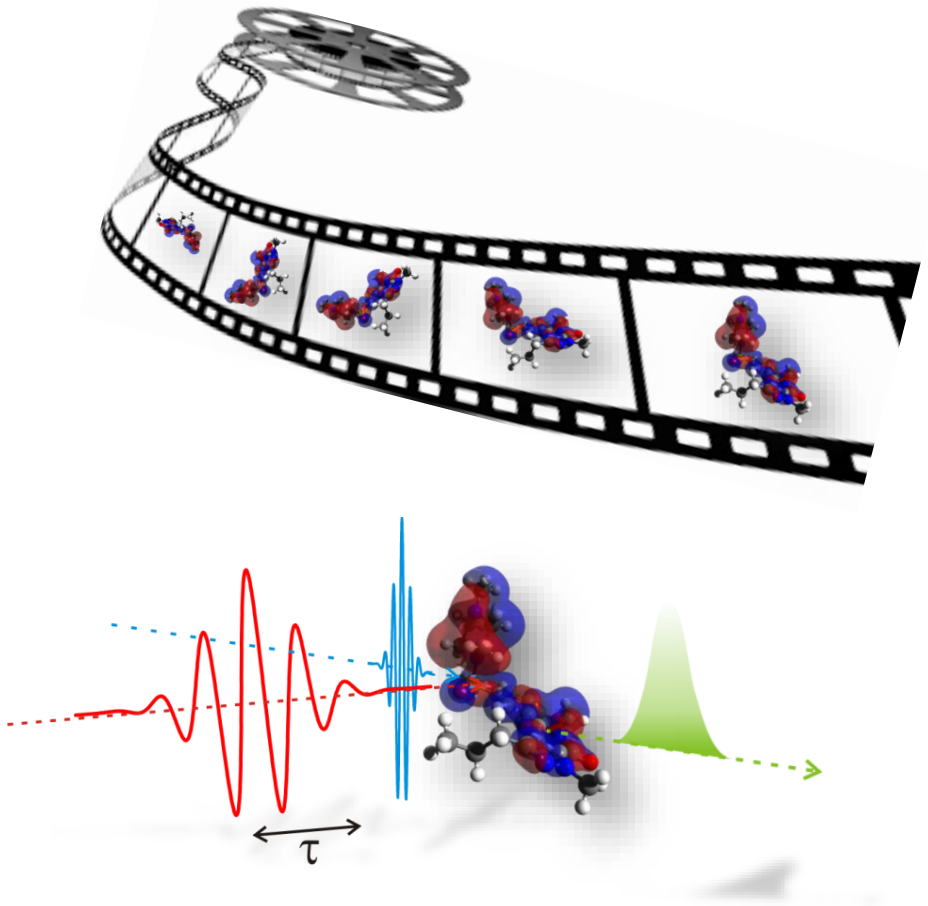
PHOTON INSTRUMENTATION IN THE EUV

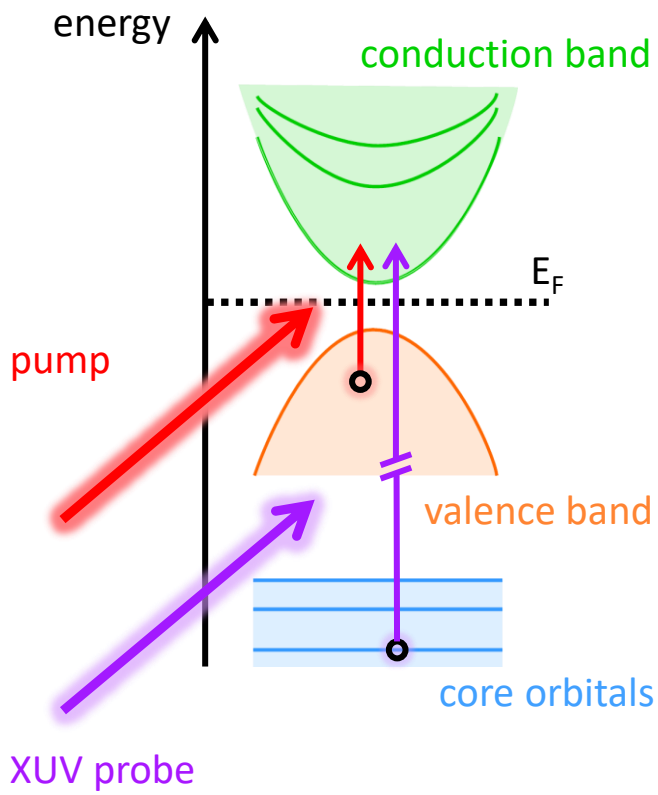
ULTRAFAST SPECTROSCOPY

STUDY AND POSSIBLY CONTROL OF ULTRAFAST DYNAMICS FROM ATOMS TO SOLIDS



ULTRAFAST SPECTROSCOPY: METHODOLOGY





ULTRAFAST SPECTROSCOPY: "PUMP-PROBE" APPROACH

WHY ULTRAFAST SPECTROSCOPY IN THE SOFT X-RAYS?

EUV AND SOFT-X ELECTROMAGNETIC SPECTRUM

EXTREME ULTRAVIOLET (EUV OR XUV):

from 124 nm to 10 nm (10 eV up to 124 eV)

SOFT X-RAYS:

from 10 nm to 0,2 nm (124 eV to 5 keV)

HARD X-RAYS:

above 5–10 keV, below 0.2–0.1 nm wavelength

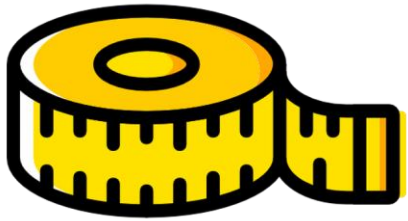
WATER WINDOW:

region of the electromagnetic spectrum in which water is transparent to soft x-rays
From the K-absorption edge of carbon at 282 eV (4.40 nm) to the K-edge of oxygen at 533 eV (2.33 nm wavelength)

SOURCE: WIKIPEDIA

PROPERTIES OF SOFT-X

✓ HIGH SPATIAL RESOLUTION

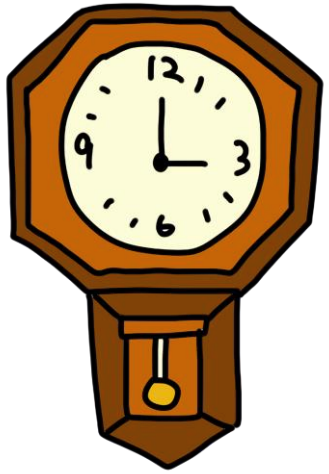


WAVELENGTH SCALE:

CARBON K-EDGE 280 EV (44 ANGSTROMS)

BOND LENGTH IN METHANE 1 ANGSTROMS

✓ HIGH TEMPORAL RESOLUTION



TIME SCALE:

BOHR ORBITAL PERIOD IN HYDROGEN ATOM 150 AS

HYDROGEN MOLECULES VIBRATIONAL PERIOD 8 FS

✓ CHEMICAL SENSITIVITY

FOCUS ON INDIVIDUAL ATOMS WITHIN MOLECULES TO STUDY ELECTRONIC AND NUCLEAR DYNAMICS ON THEIR INTRINSIC SCALES (ATTOSECOND AND ANGSTROMS)

THE IDEAL SOURCE

- ✓ BROADBAND X-RAY CONTINUUM FOR CHEMICAL SENSITIVITY
- ✓ FULL POLARIZATION CONTROL
- ✓ EXTREME TEMPORAL RESOLUTION
- ✓ HIGH BRIGHTNESS

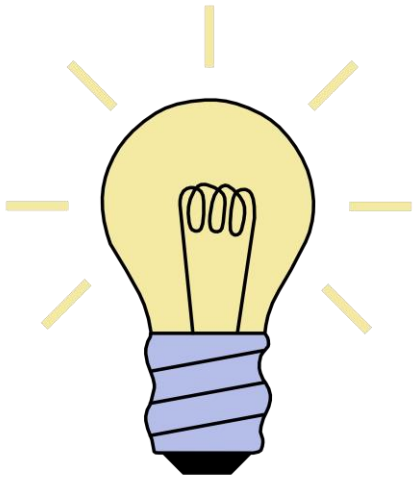
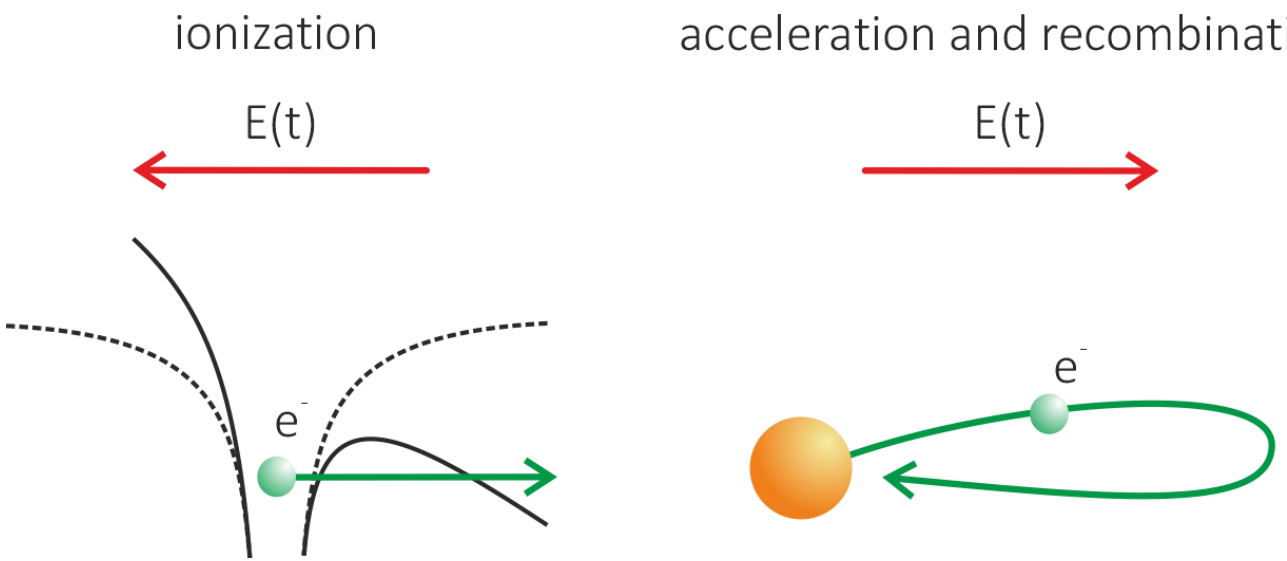


TABLE-TOP SOURCES vs FREE ELECTRON LASERS

- PRICE
- FLEXIBILITY
- TEMPORAL RESOLUTION (50 AS)
- ACCESSIBILITY
- STRUCTURED LIGHT

- INTENSITY (10^{20} W/CM^2)
- INSTRUMENTATION
- SPECTRAL PURITY
- POLARIZATION CONTROL

HIGH ORDER HARMONIC GENERATION

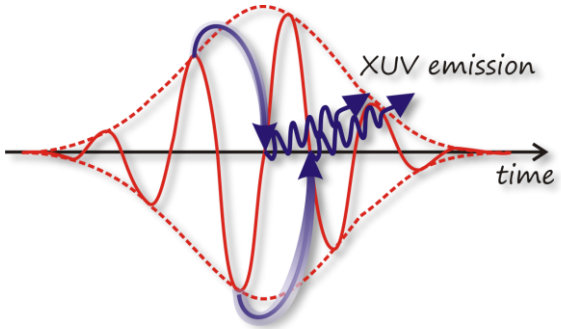


I. THE LASER FIELD DETACHES AN ELECTRON FROM THE VALENCE SHELL BY TUNNEL IONIZATION

II. THE FREE ELECTRON IS ACCELERATED BY THE LASER FIELD

III. THE ENERGY GAINED BY THE ELECTRON IS RELEASED THROUGH THE EMISSION OF A XUV PHOTON

HIGH ORDER HARMONIC GENERATION

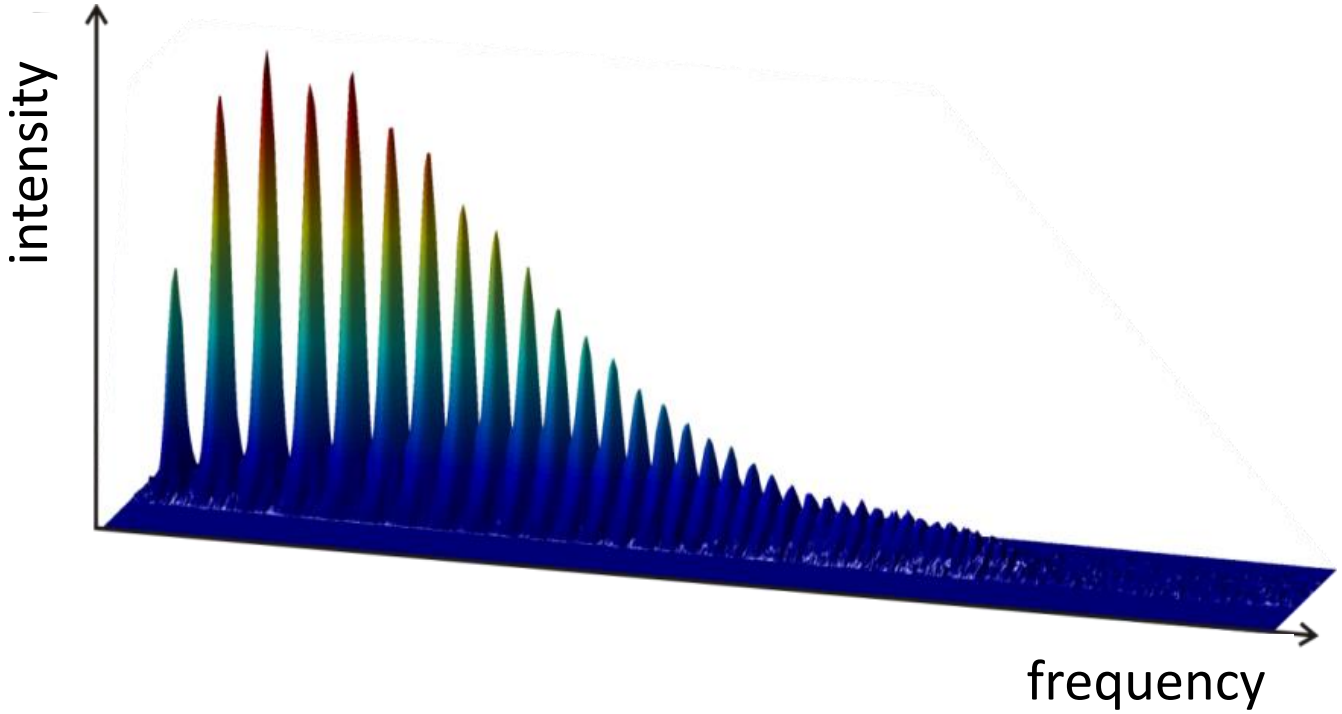


$H\omega_{CUTOFF} = I_P + 3.17\ U_P$

$U_P \sim E^2\lambda^2$

ODD HARMONICS OF THE FUNDAMENTAL FREQUENCY

TRAIN OF ATTOSECOND PULSES

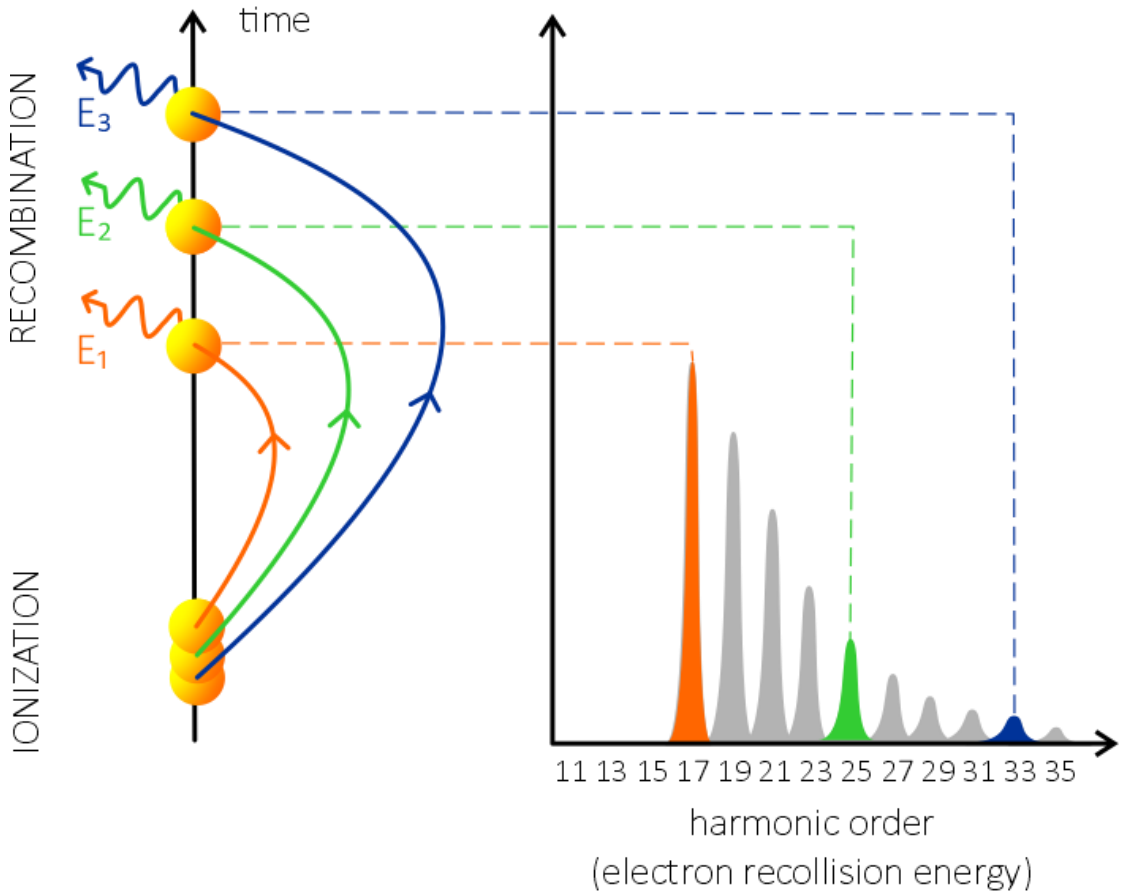


HOW TO INCREASE THE HHG CUTOFF

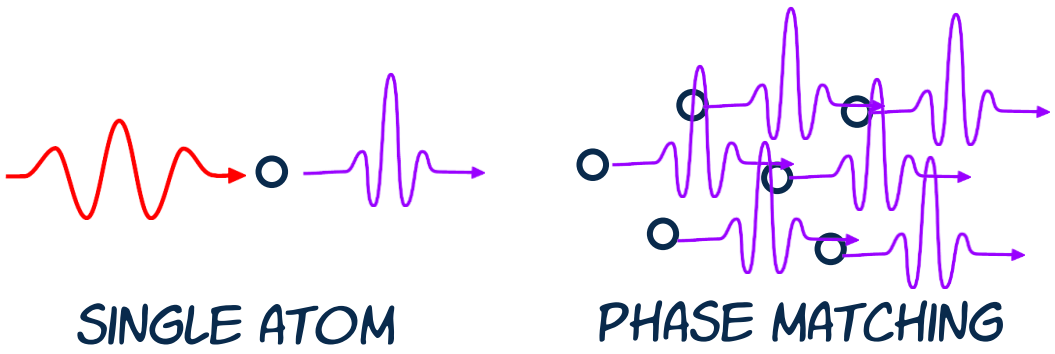
- INCREASE I_p
- INCREASE THE DRIVING INTENSITY
- INCREASE THE DRIVING WAVELENGTH

LARGER WAVEPACKET DIFFUSION

→ LOWER RECOMBINATION PROBABILITY



PHASE MATCHING IN HHG



SINGLE ATOM

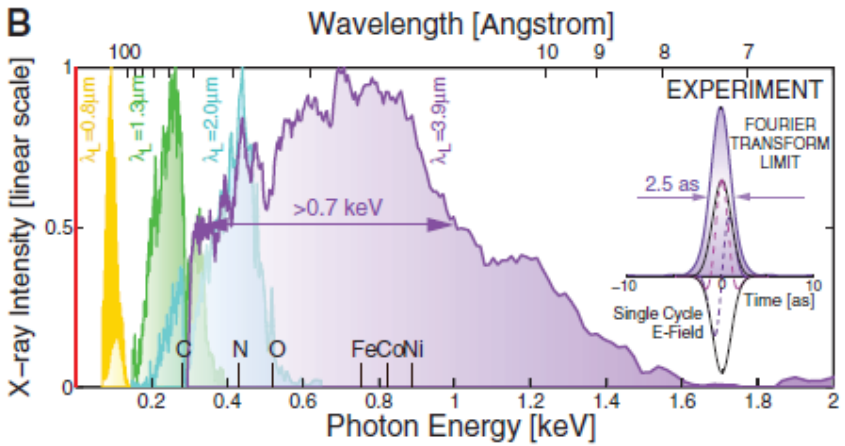
PHASE MATCHING

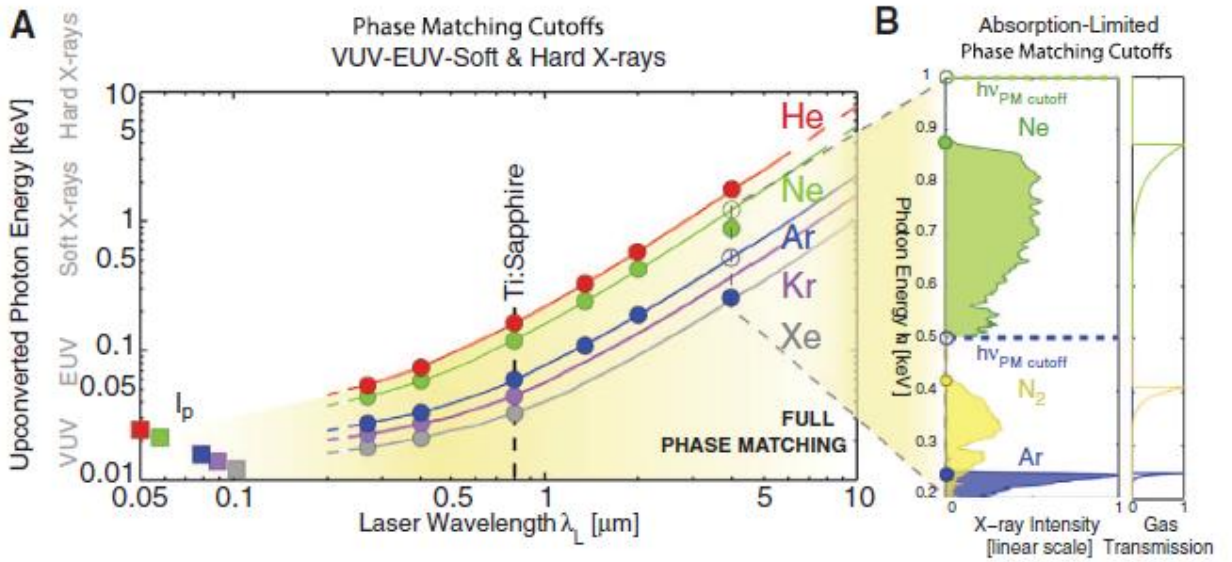
- PHASE-MATCHING DEPENDS ON:
- GAS MEDIUM
- DRIVING WAVELENGTH/INTENSITY
- GEOMETRY OF THE INTERACTION

PHASE MATCHING IN HHG DRIVEN BY LONG WAVELENGTH

Bright Coherent Ultrahigh Harmonics in the keV X-ray Regime from Mid-Infrared Femtosecond Lasers

Tenio Popmintchev,[1*] Ming-Chang Chen,[1] Dimitar Popmintchev,[1] Paul Arpin,[1] Susannah Brown,[1] Skirmantas Ališauskas,[2] Giedrius Andriukaitis,[2] Tadas Balčiunas,[2] Oliver D. Mücke,[2] Audrius Pugzlys,[2] Andrius Baltuška,[2] Bonggu Shim,[3] Samuel E. Schrauth,[3] Alexander Gaeta,[3] Carlos Hernández-García,[4] Luis Plaja,[4] Andreas Becker,[1] Agnieszka Jaron-Becker,[1] Margaret M. Murnane,[1] Henry C. Kapteyn[1]

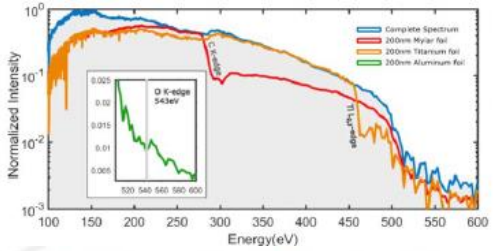


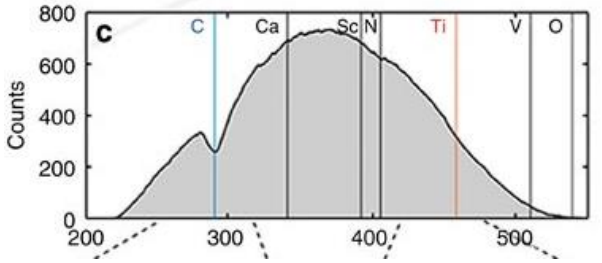


T. POPMINTCHEV ET AL., SCIENCE 336, 1287 (2012)

TABLE-TOP SOFT X-RAYS SOURCES
STATE OF THE ART

WATER WINDOW HHG SOURCES





BIEGERT: S.M. TEICHMANN ET AL., NATURE COMM. 7, 11493 (2016)

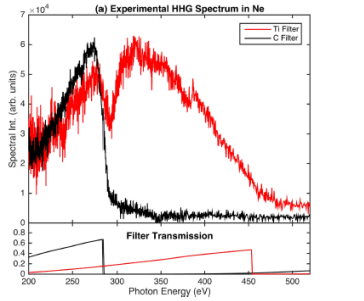
LEGARE: V. CARDIN ET AL., J. PHYS. B: 51 174004 (2018)

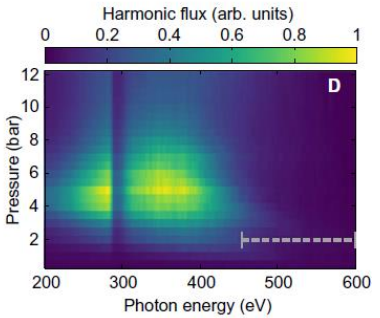
KAERTNER: G. STEIN ET AL., J. PHYS. B: 49 155601 (2016)

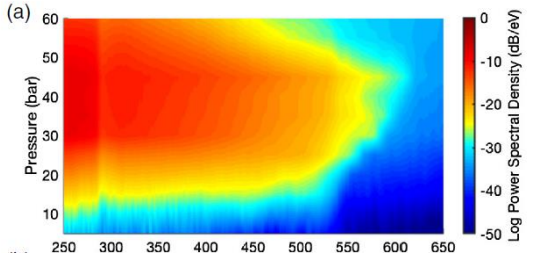
MARANGOS: JOHNSON ET AL., SCI. ADV. 4, EAAR3761 (2018)

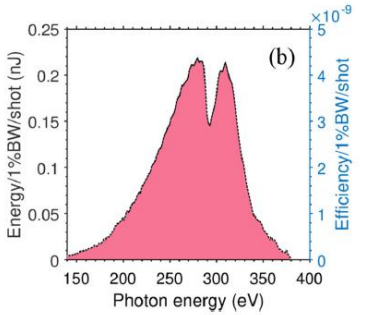
KELLER: J. PUPEIKIS ET AL., OPTICA 7, 168 (2020)

TAKAHASHI: Y. FU ET AL., COMMUNICATION PHYSICS (2020)







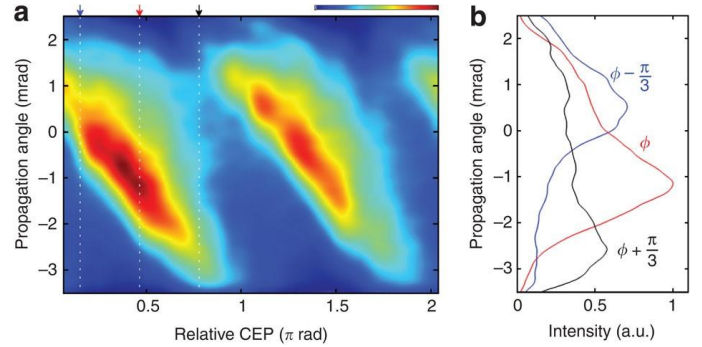


SOFT-X ATTOSECOND SOURCES

GROUP OF JENS BIEGERT

ISOLATION OF INDIVIDUAL ATTOSECOND PULSES AT THE CARBON K-EDGE BY WAVEFRONT ROTATION PULSE DURATION BELOW 400 AS AND WITH A BANDWIDTH SUPPORTING A 30-AS PULSE DURATION

FRANCISCO SILVA ET AL., NATURE COMM. 6, 6611 (2015)



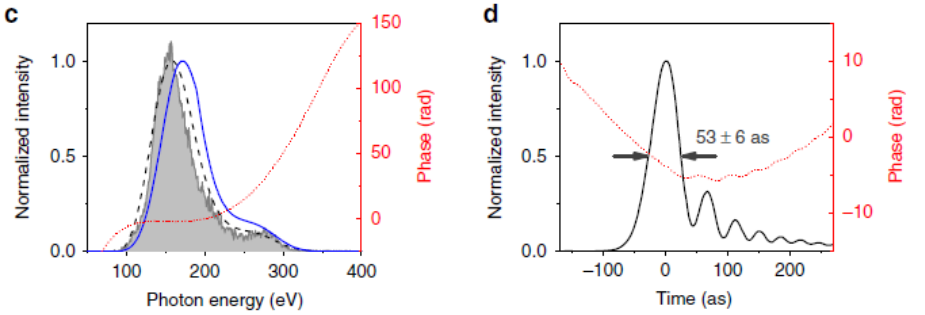
GROUP OF ZENGHU CHANG

2-CYCLE OPA AT 1800 NM, POLARIZATION GATING

53 AS, 200 EV BANDWIDTH UP TO THE CARBON K-EDGE

PROOF METHOD FOR THE TEMPORAL CHARACTERIZATION

J. LI ET AL., NATURE COMMUNICATION DOI: 10.1038/S41467-017-00321-0 (2017)



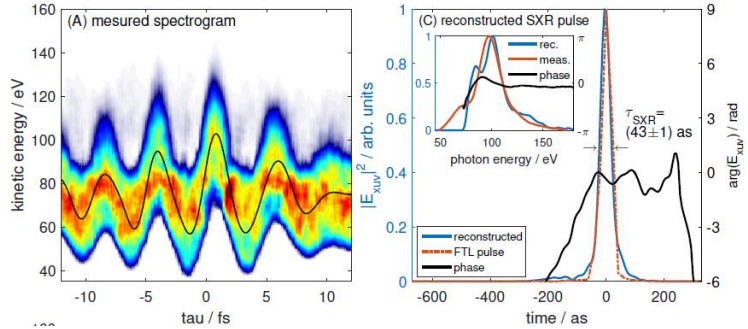
GROUP OF HANS JAKOB WOERNER

2-CYCLE OPA @ 1800 NM, AMPLITUDE GATING

43-ATTOSECOND

100 EV BANDWIDTH REACHING PHOTON ENERGIES UP TO 180 EV

T. GAUMNITZ ET AL., OPTICS EXPRESS 25, 27516 (2017)



TRANSIENT ABSORPTION IN THE WATER WINDOW

BIEGERT:

B. BUADES ET AL., APPL. PHYS. REV. 8, 011408 (2021)

LEONE:

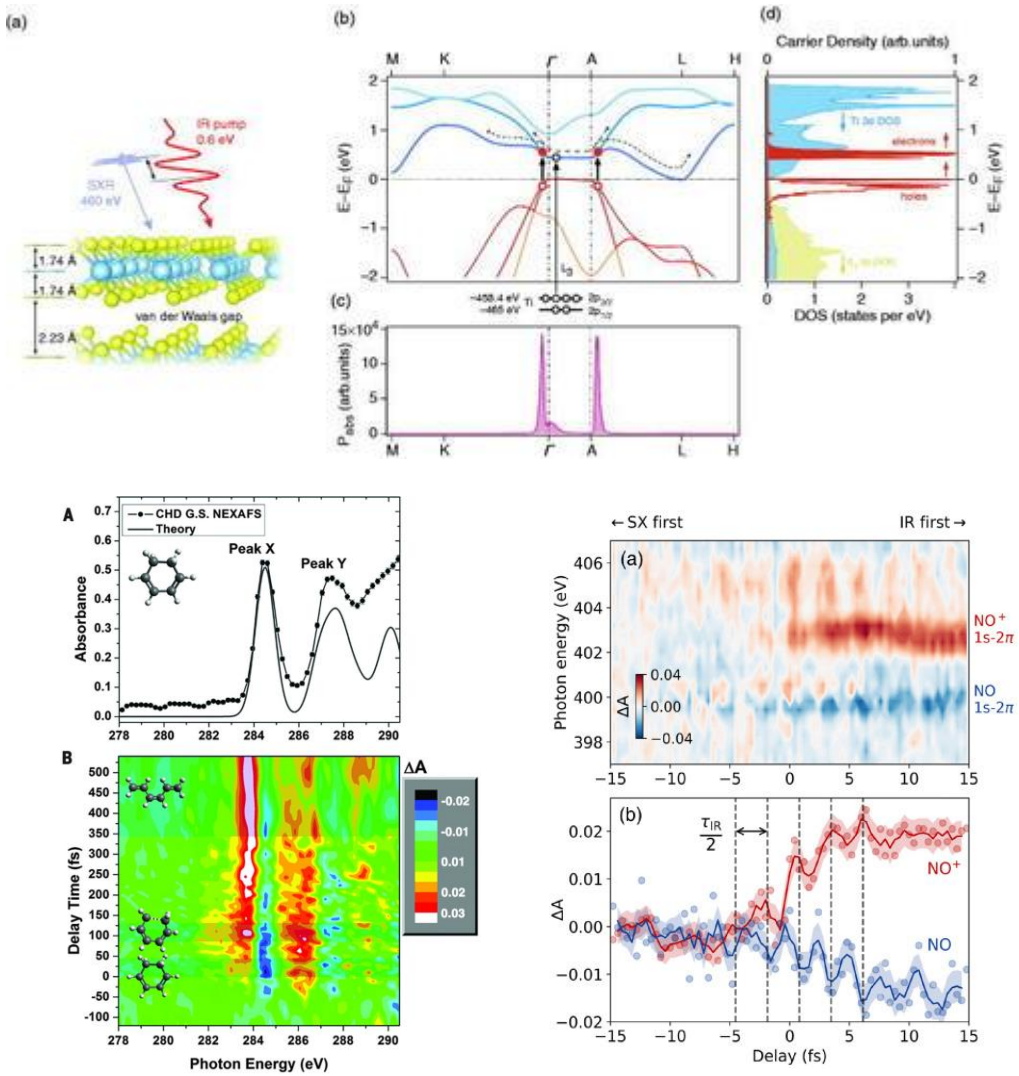
A. R. ATTAR ET AL., SCIENCE 356, 54 (2017)

ITATANI:

N. SAITO ET AL., OPTICA 6, 1542-1546 (2019)

WOERNER:

Y. PERTOT ET AL. SCIENCE 355, 264 (2017)

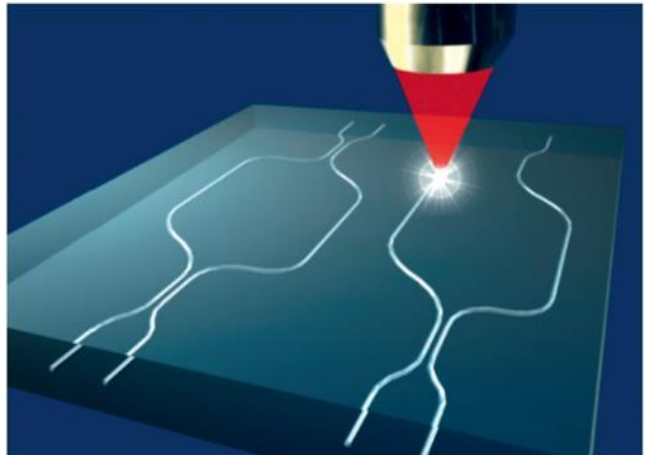


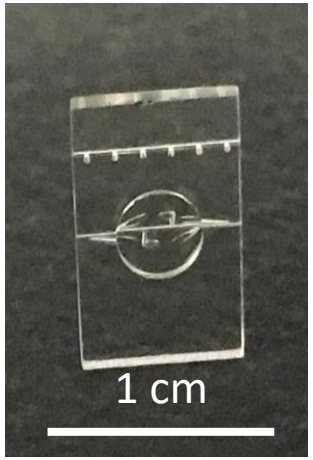
NOVEL STRATEGY FOR THE GENERATION OF BRIGHT ATTOSECOND PULSES IN THE SOFT-X: HHG IN A CHIP

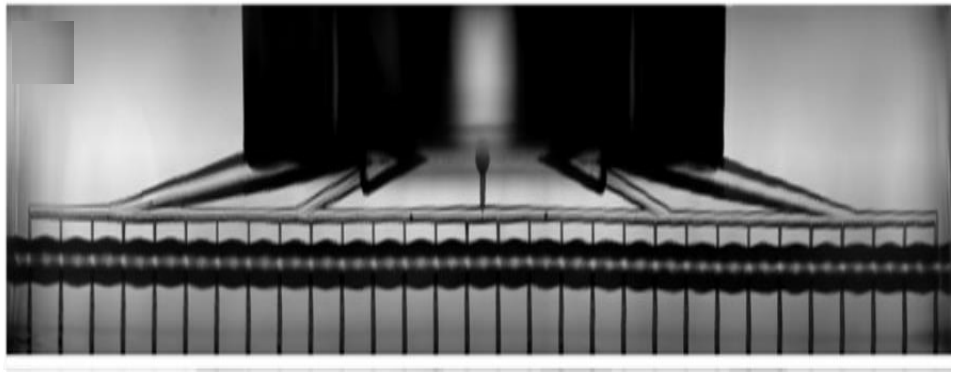
THE IDEA: HHG + MICROFLUIDIC

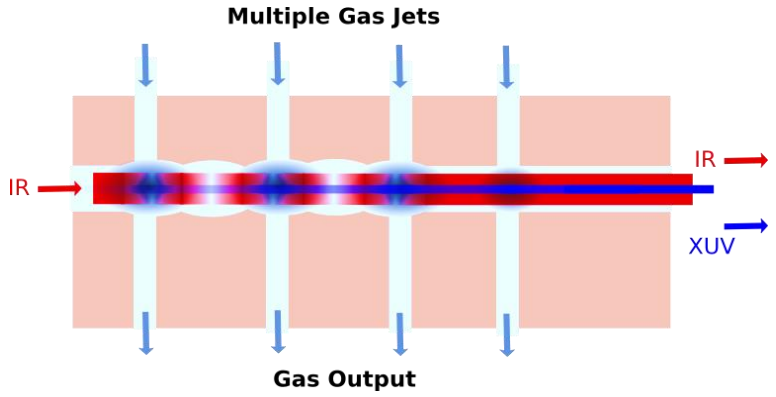
FEMTOSECOND LASER IRRADIATION FOLLOWED BY CHEMICAL ETCHING

BY R. MARTINEZ VAZQUEZ + R. OSELLAME





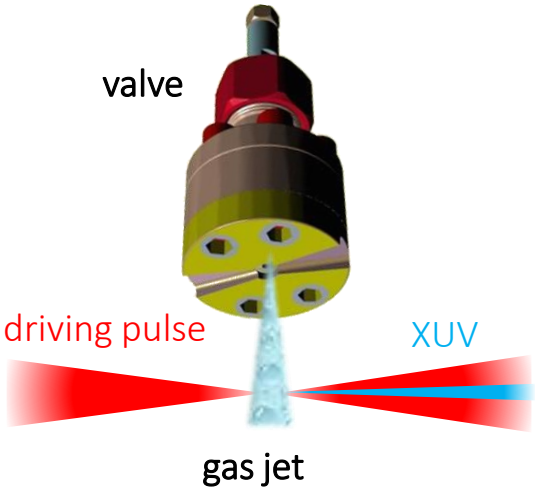




- ✓ FLEXIBLE PLATFORM
- ✓ INCREASED EFFICIENCY
- ✓ EXTENDED BANDWIDTH
- ✓ POLARIZATION MANIPULATION (?)

THE IDEA: HHG + MICROFLUIDIC

gas jet

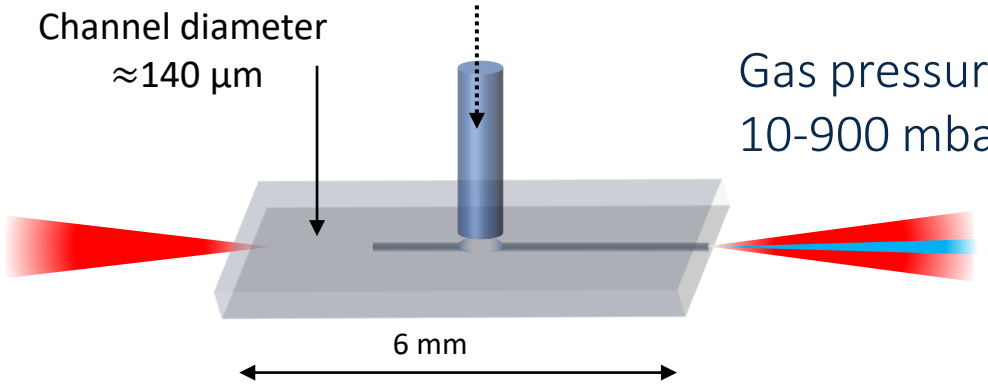


Gas jet dimension
~ hundreds-µm

Gas backing pressure:
> 1bar

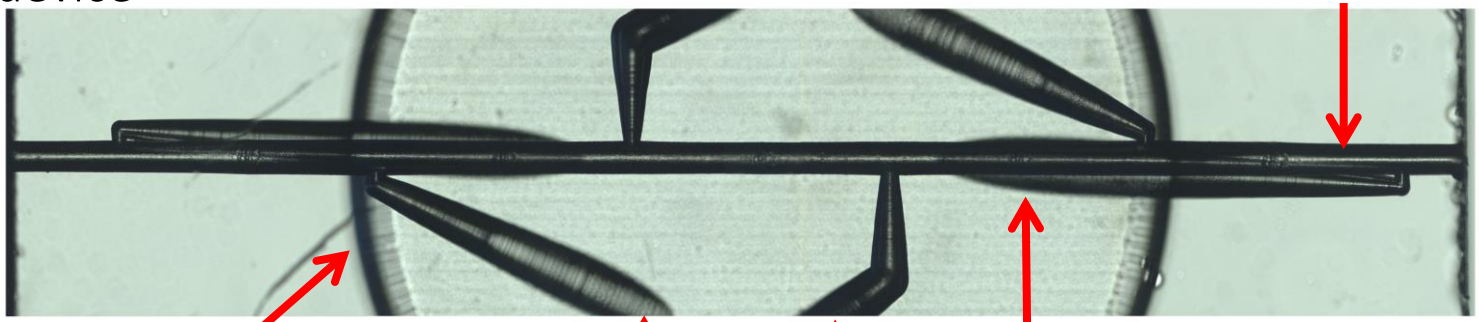
Gas-filled chip

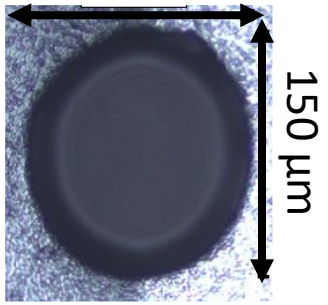
Continuus flow



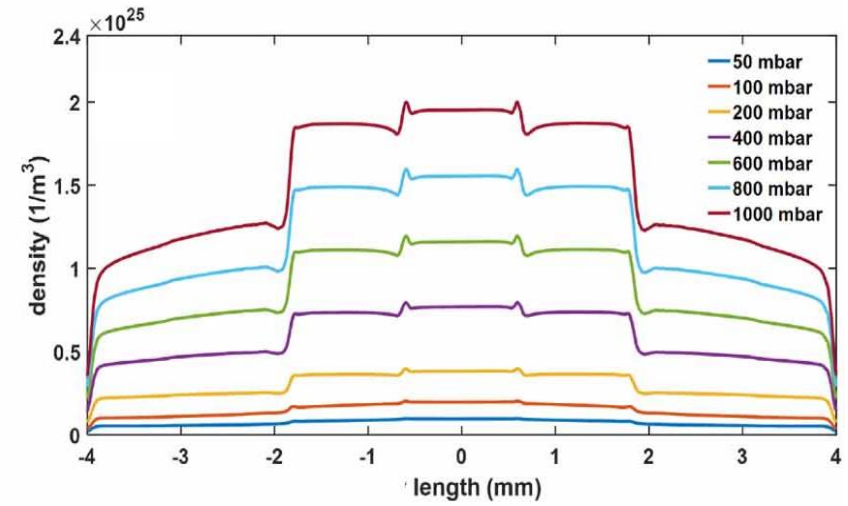
Gas pressure:
10-900 mbar

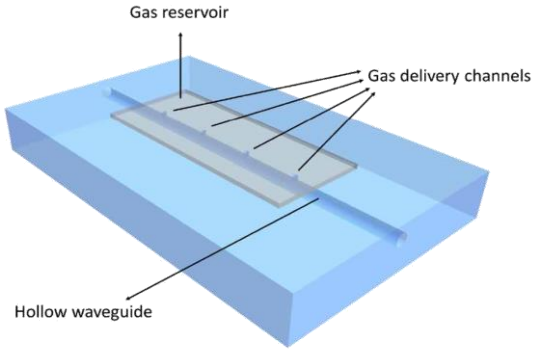
Top view of the device



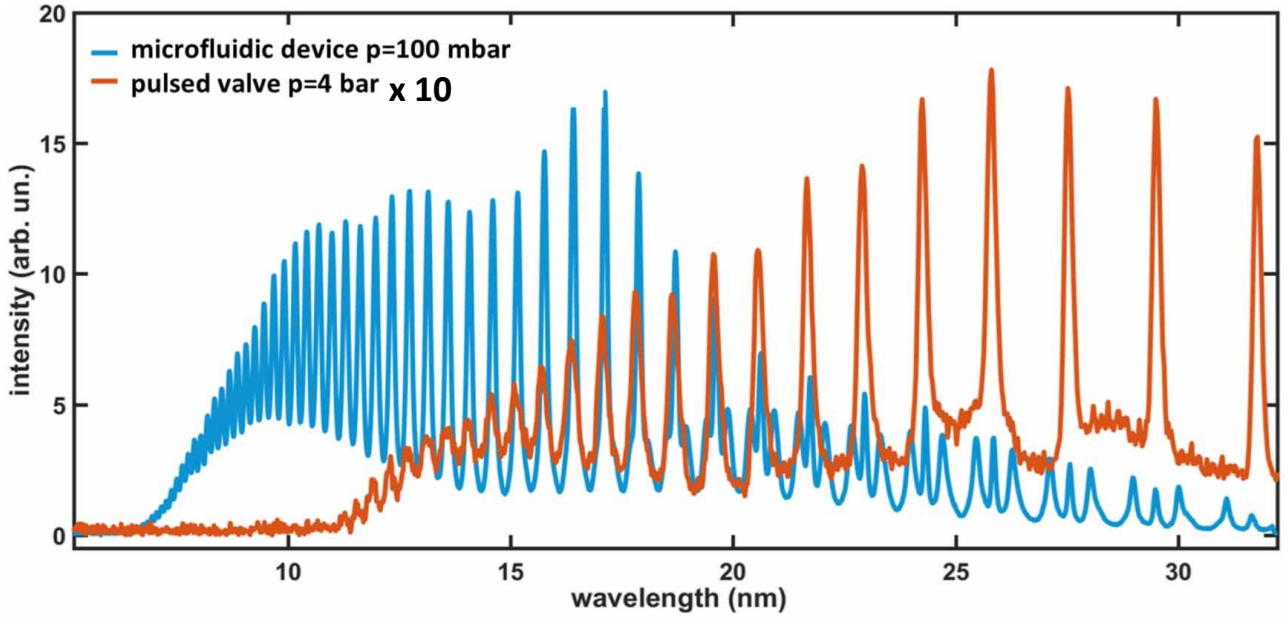


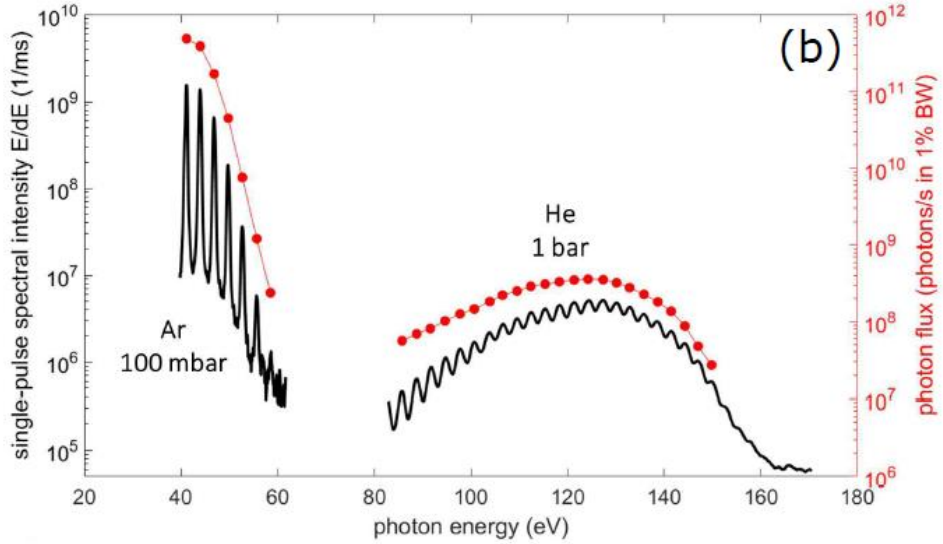
CHIP VS PULSED VALVE





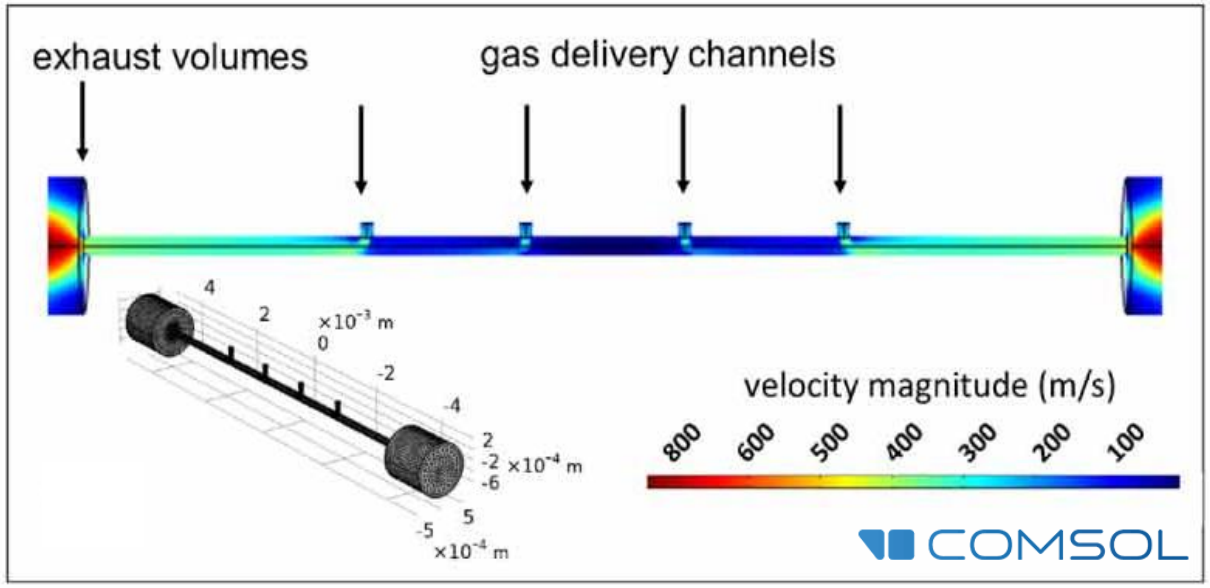
HE, 800 NM, 20 FS, SAME PULSE ENERGY, SINGLE SHOT

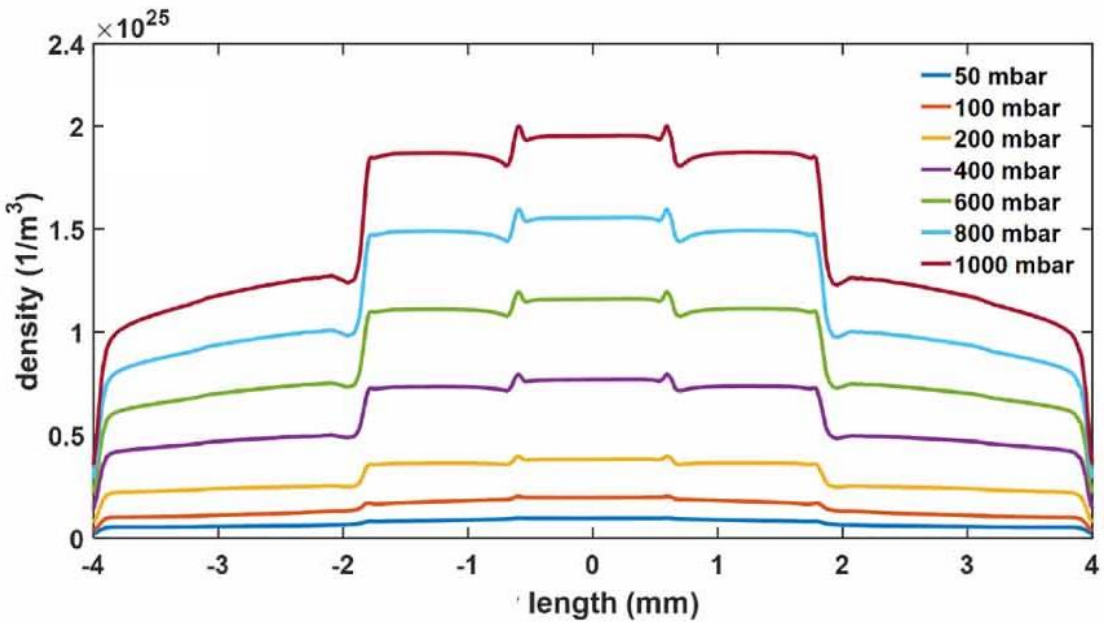




A.G. CIRIOLO ET AL., J. PHYS. PHOTONICS 2, 024005 (2020)

HHG IN CHIP: GAS DENSITY PROFILE

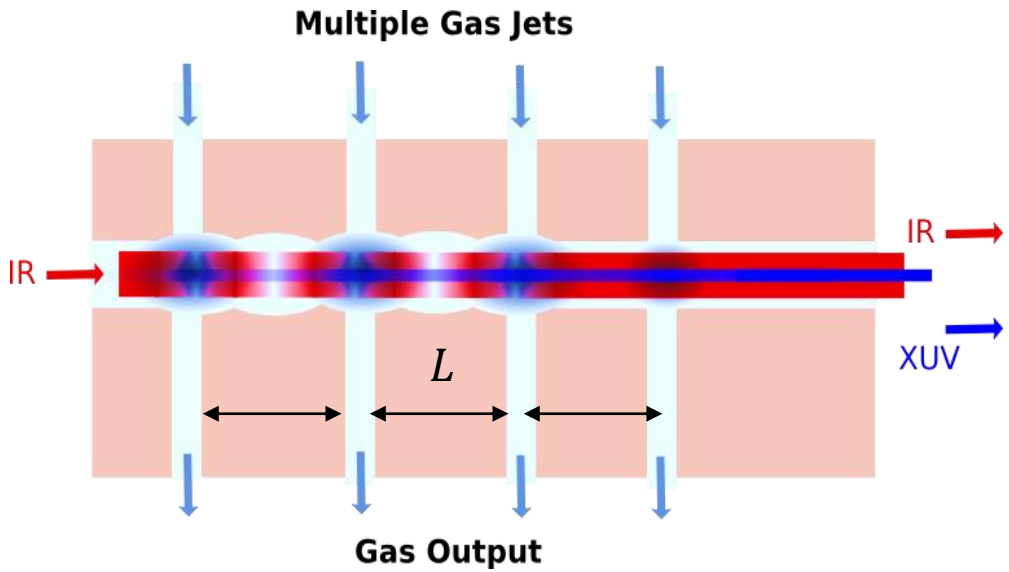




A.G. CIRIOLO ET AL., J. PHYS. PHOTONICS 2, 024005 (2020)

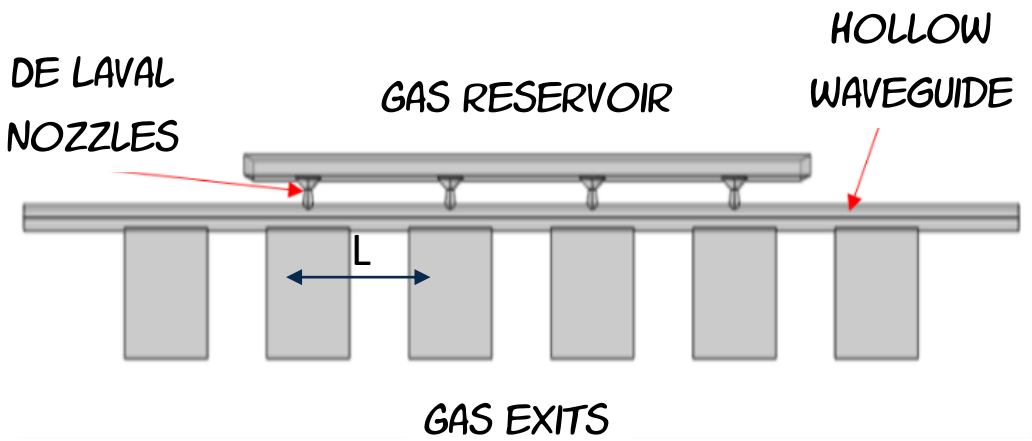
CHIP ENGINEERING

PHASE MATCHING OPTIMIZATION

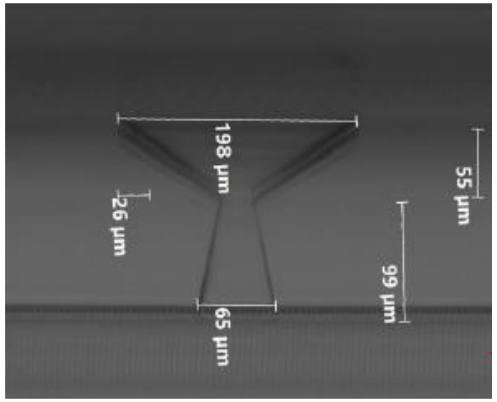


- ✓ PERIODICITY OF NOZZLES
- ✓ DIAMETER MODULATION
- ✓ NOZZLE SHAPE AND DIMENSION

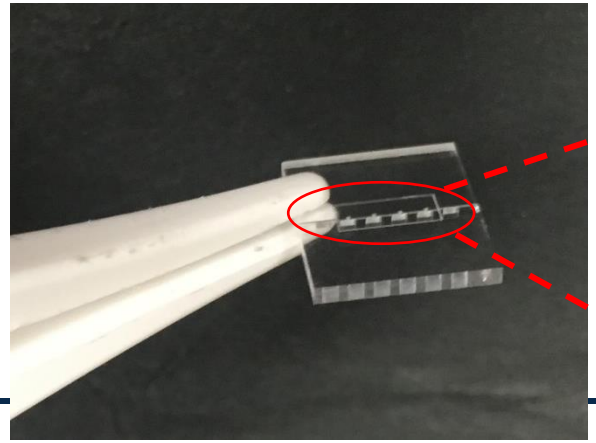
MODULATION OF GAS DENSITY



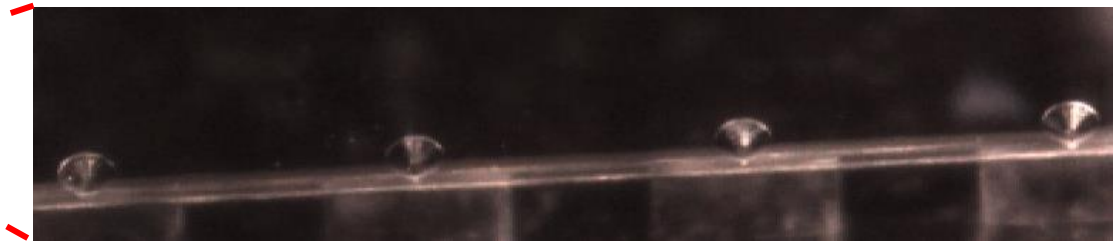
MICROSCOPE VIEW



DE LAVAL MICRO-NOZZLES

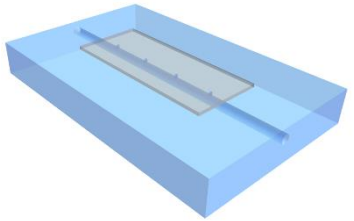


MICROSCOPE VIEW



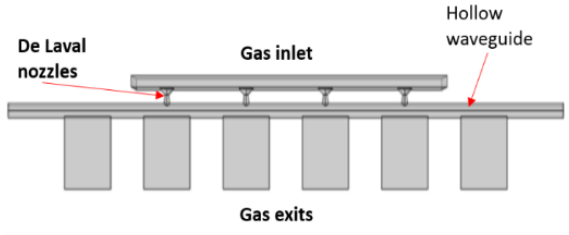
HHG IN NEW CHIP

First generation



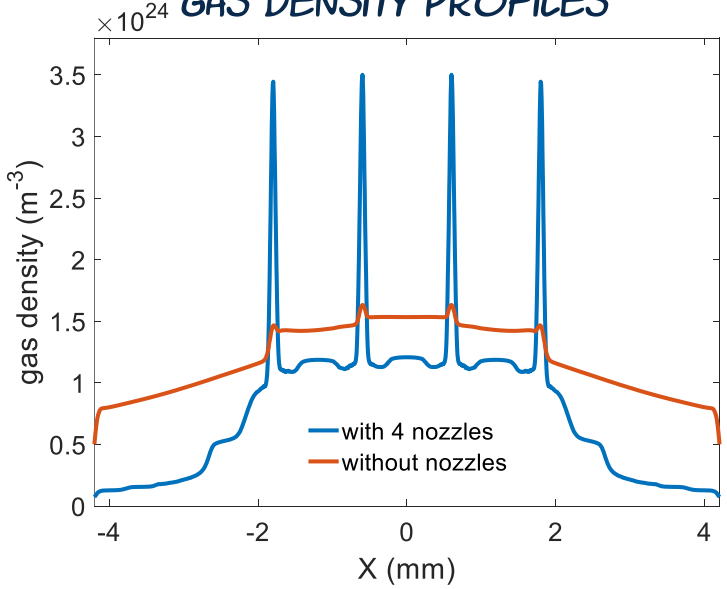
straight channels

Second generation 1.0

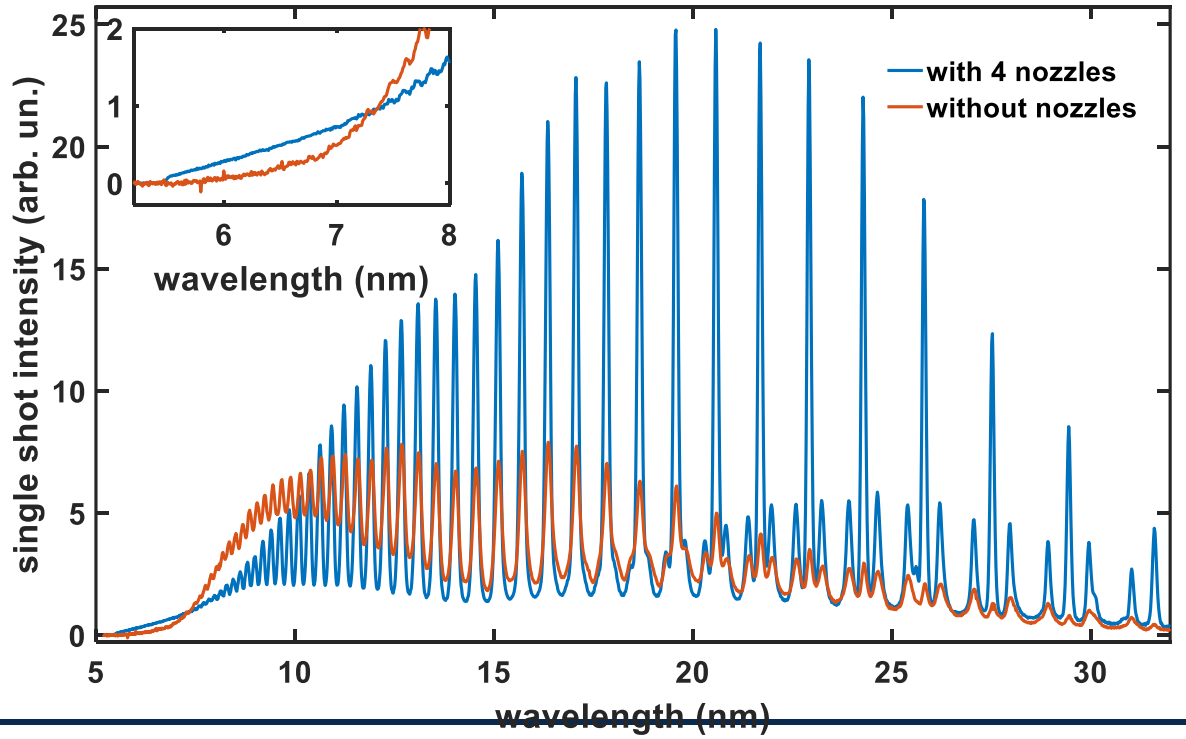


with 4 nozzles

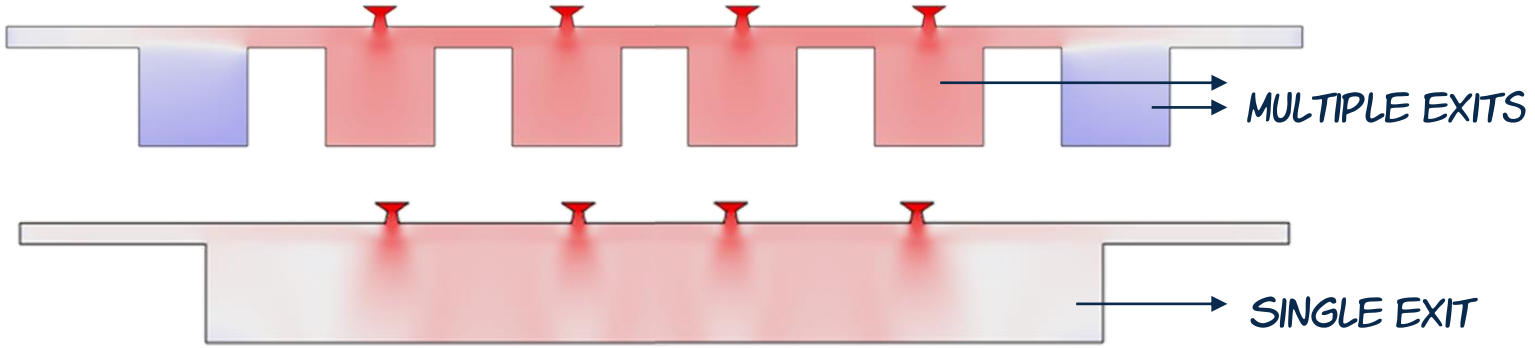
GAS DENSITY PROFILES

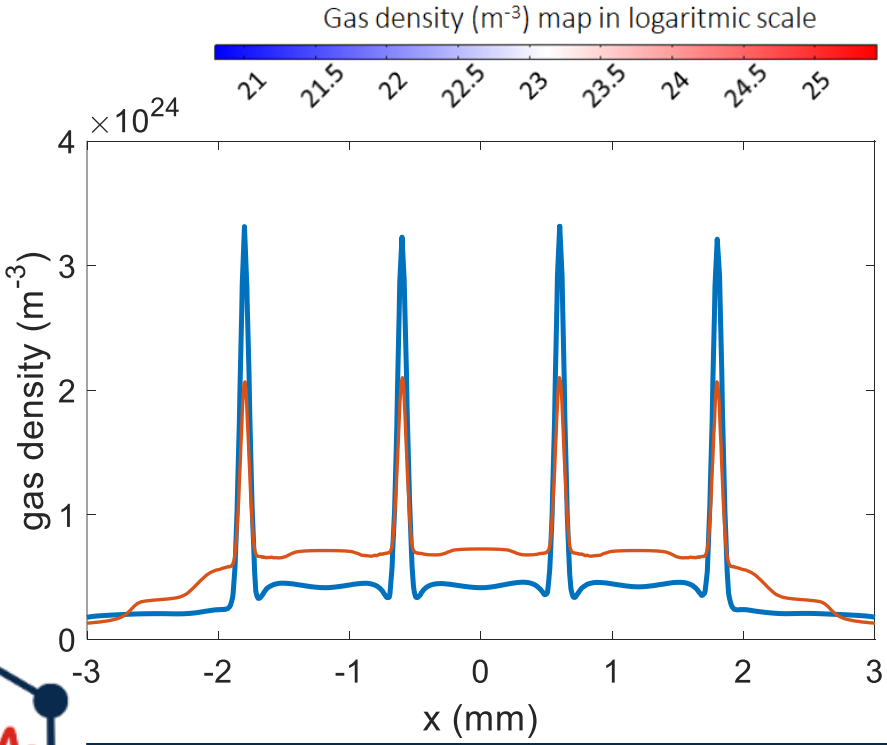


HE, 800 NM, 20 FS, SINGLE SHOT

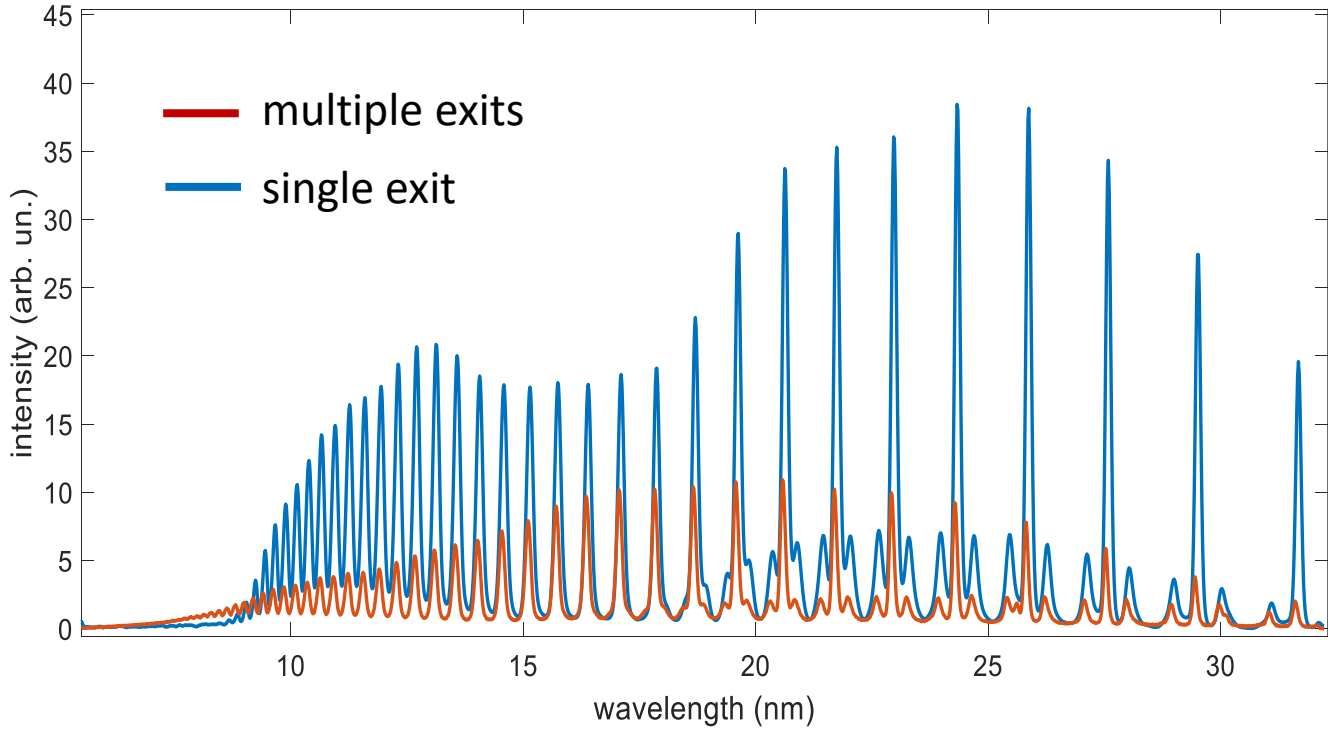


HOW TO IMPROVE THE GAS DENSITY MODULATION





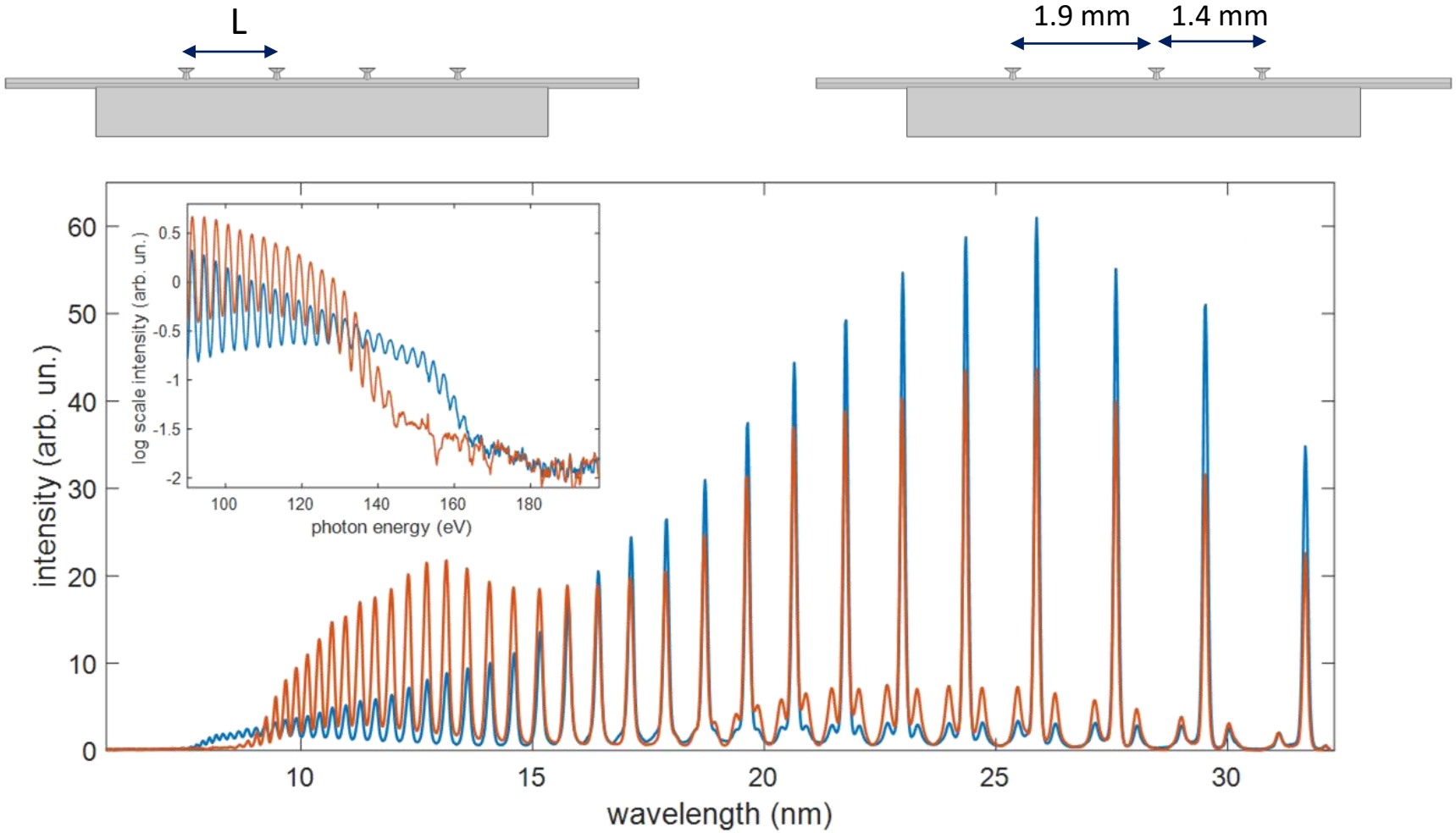
HE GAS, SINGLE SHOT



HOW TO SHAPE THE HHG

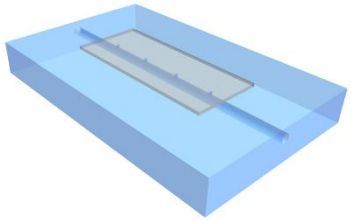
4 NOZZLES ARRANGED IN A PERIODIC STRUCTURE (L=1.2 MM)

3 NOZZLES ARRANGED IN A NON-PERIODIC STRUCTURE

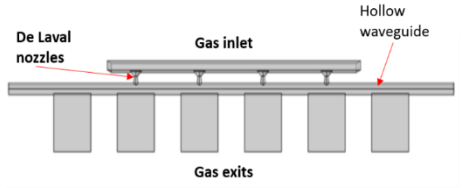


HHG IN CHIP: SUMMARY

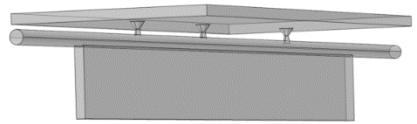
FIRST GENERATION



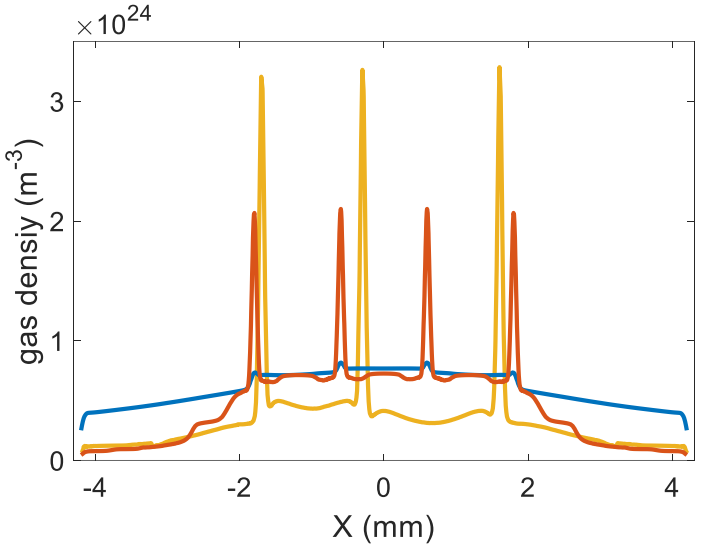
SECOND GENERATION 1.0



SECOND GENERATION 2.0

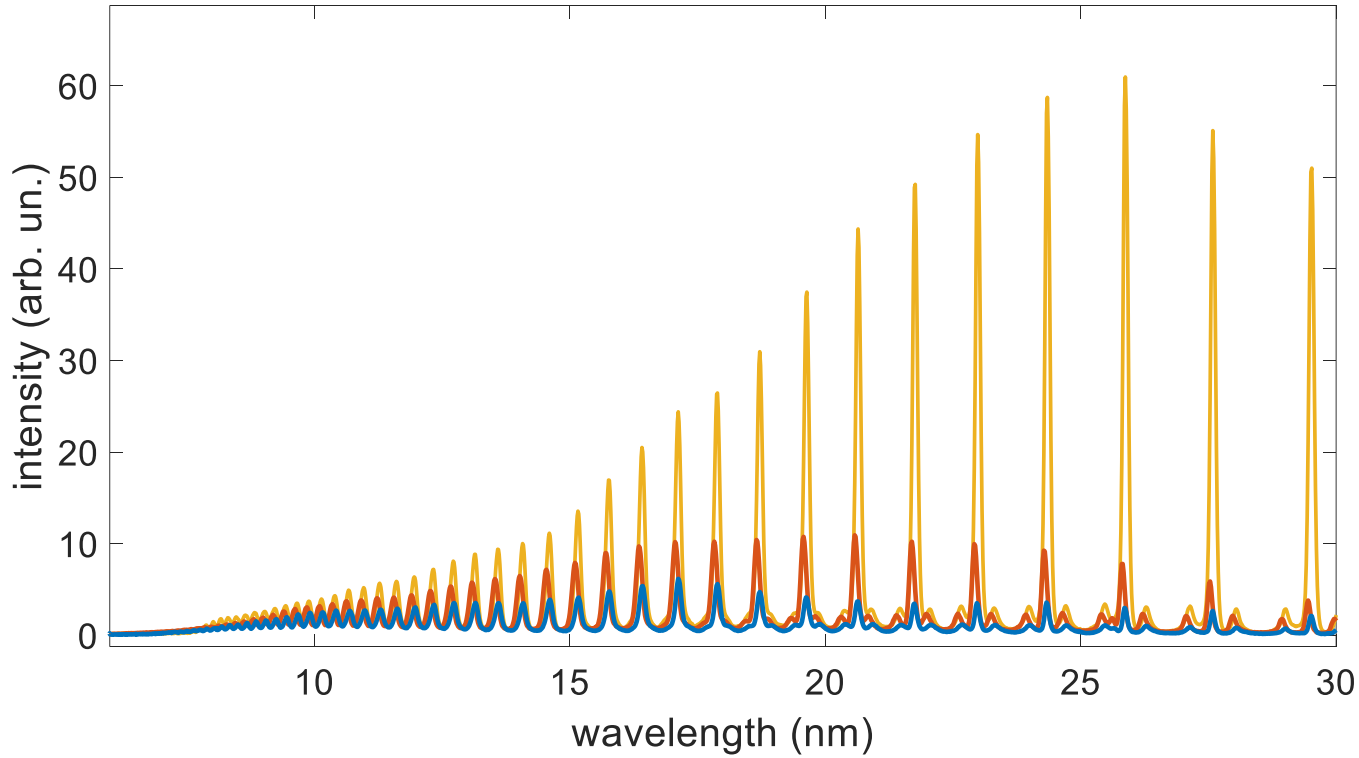


GAS DENSITY PROFILES



(SAME BACKGROUND PRESSURE)

HE GAS, SINGLE SHOT



THE ULTRAFAST DYNAMIC IN MATTER GROUP

SALVATORE STAGIRA

EUGENIO CINQUANTA

MICHELE DEVETTA

EGLE MOLOTOKAITE

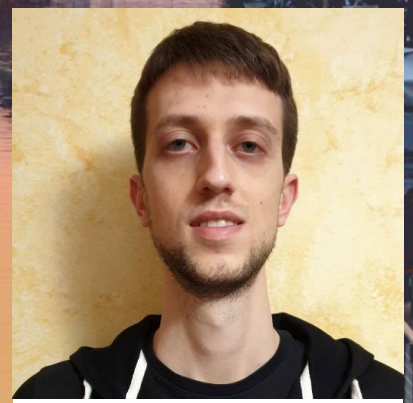
DAVIDE FACCIALA'

ANNA G CIRIOLO

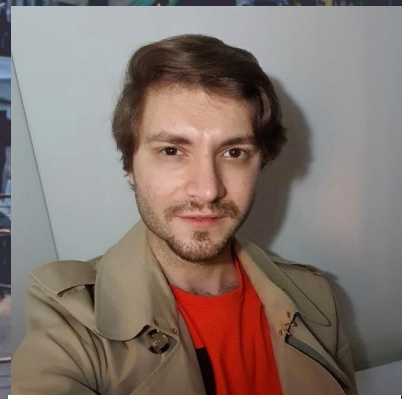
ANDREA ANNUNZIATA

MATTEO BONANOMI

GABRIELE CRIPPA



LORENZO GATTO



BOGDAN ISPAS

STAVROULA VOVLA

CNR IFN
Istituto di Fotonica e Nanotecnologie

POLITECNICO MILANO 1863

ACKNOWLEDGMENTS

H2020-INFRAIA-2019-1 GA 871124

Cost Action CA18222

H2020-MSCA-ITN-2019 GA 860553

ERC-2018-PoC GA 813103

CNR laboratorio congiunto

MIUR International Project ELI

MIUR PRIN 2017RKWTMY

CATERINA.VOZZI@CNR.IT

WWW.UDYNI.EU

OPEN POSITIONS IN UDYNI LABS:

1 PHD POSITION (FEBRUARY 2022) ON SOFT X-RAY INTEGRATED PHOTONICS

1 POST DOC (2022) ULTRAFAST DYNAMICS IN BIOMOLECULES

Frontiers of Ultrafast X-ray Spectroscopy and Imaging

OSA Virtual Seminar

Giulia Fulvia Mancini

Department of Physics, University of Pavia (IT)

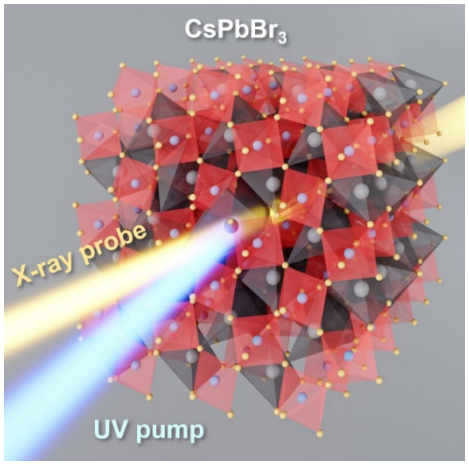
Zoom webinar

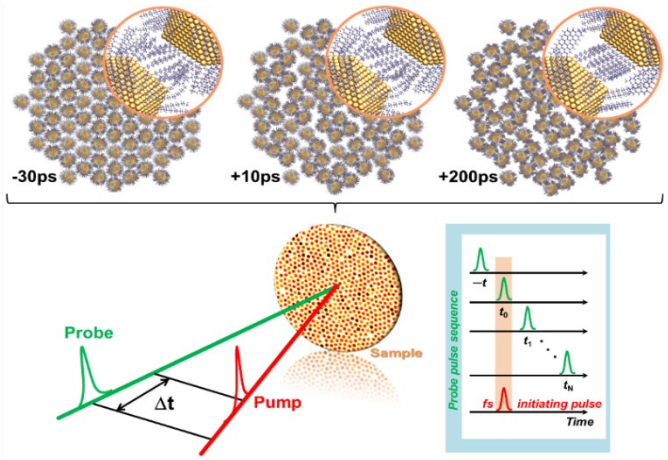
May 20th 2021

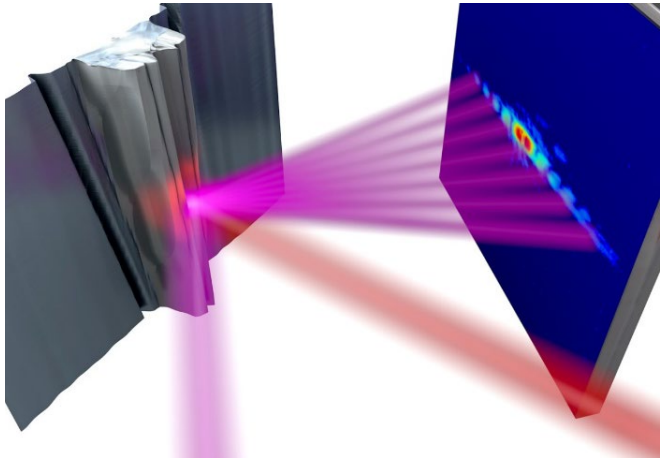
Deliverables of this webinar

Outline:

- Relevance of new functional nanomaterials
- Challenges in technology miniaturization
- Collectives from building-blocks with tailored properties
- Ultrafast techniques: general concept
- Probing heterogeneity & dimensionality:
  - Spectroscopy: Polaronic non-thermal photo-activation in CsPbBr3
  - Diffraction Imaging: mechanical stiffness in Au-NPs
  - Coherent EUV Imaging: Thermal and acoustic dynamics in waveguides

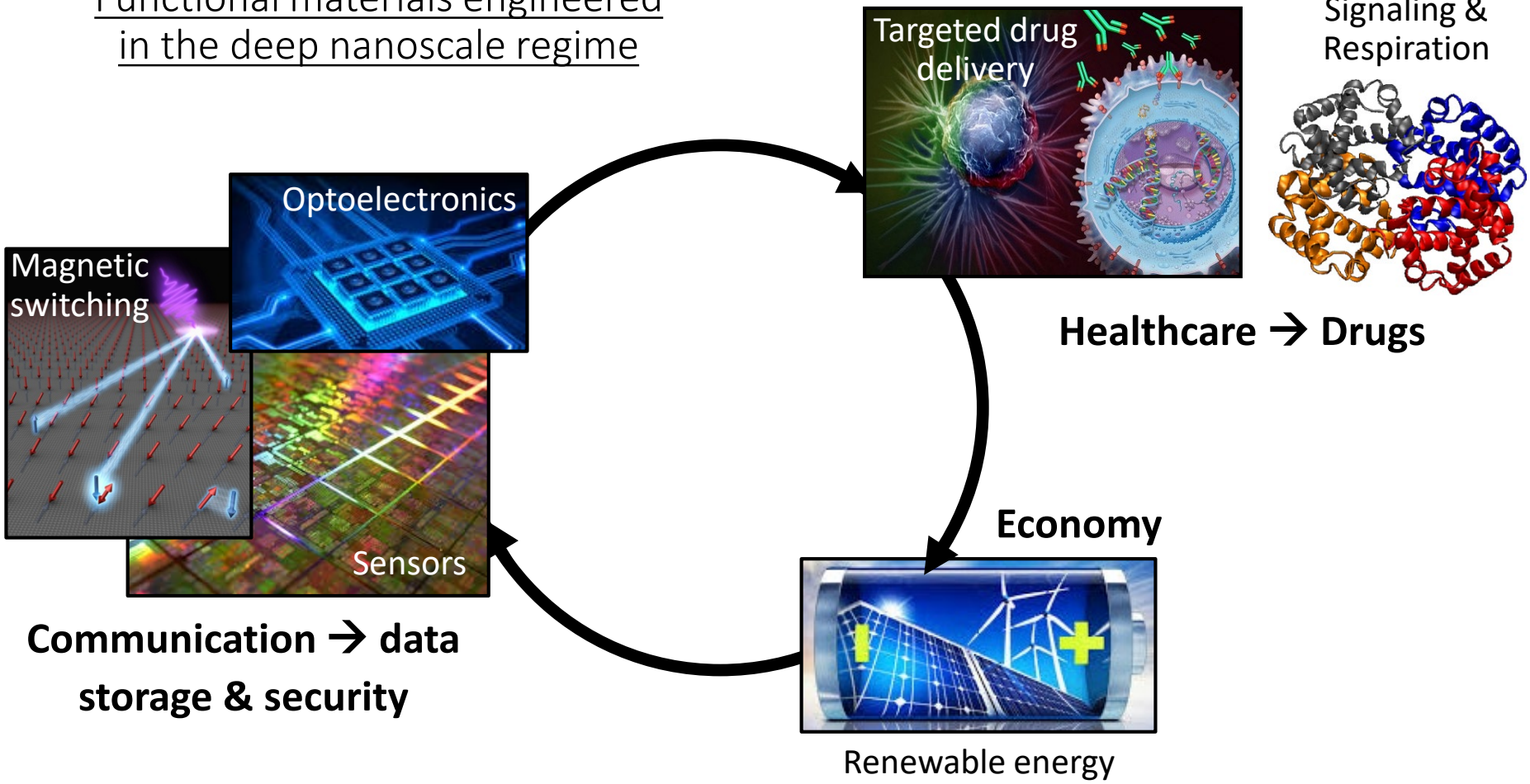






"Everything changes at the nano-level"

Technology miniaturization:
Functional materials engineered in the deep nanoscale regime



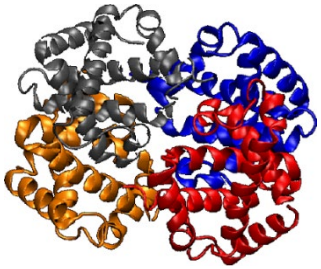
Bulk macroscopic models cannot predict heat, charge or spin transport

"Everything changes at the nano-level"

Current grand challenge:

Correlate macro- & microscopic properties *while* functionality occurs

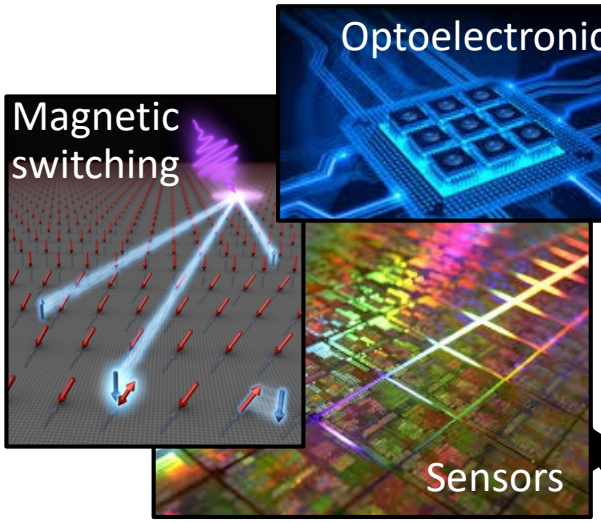
Signaling & Respiration



Healthcare → Drugs

Economy

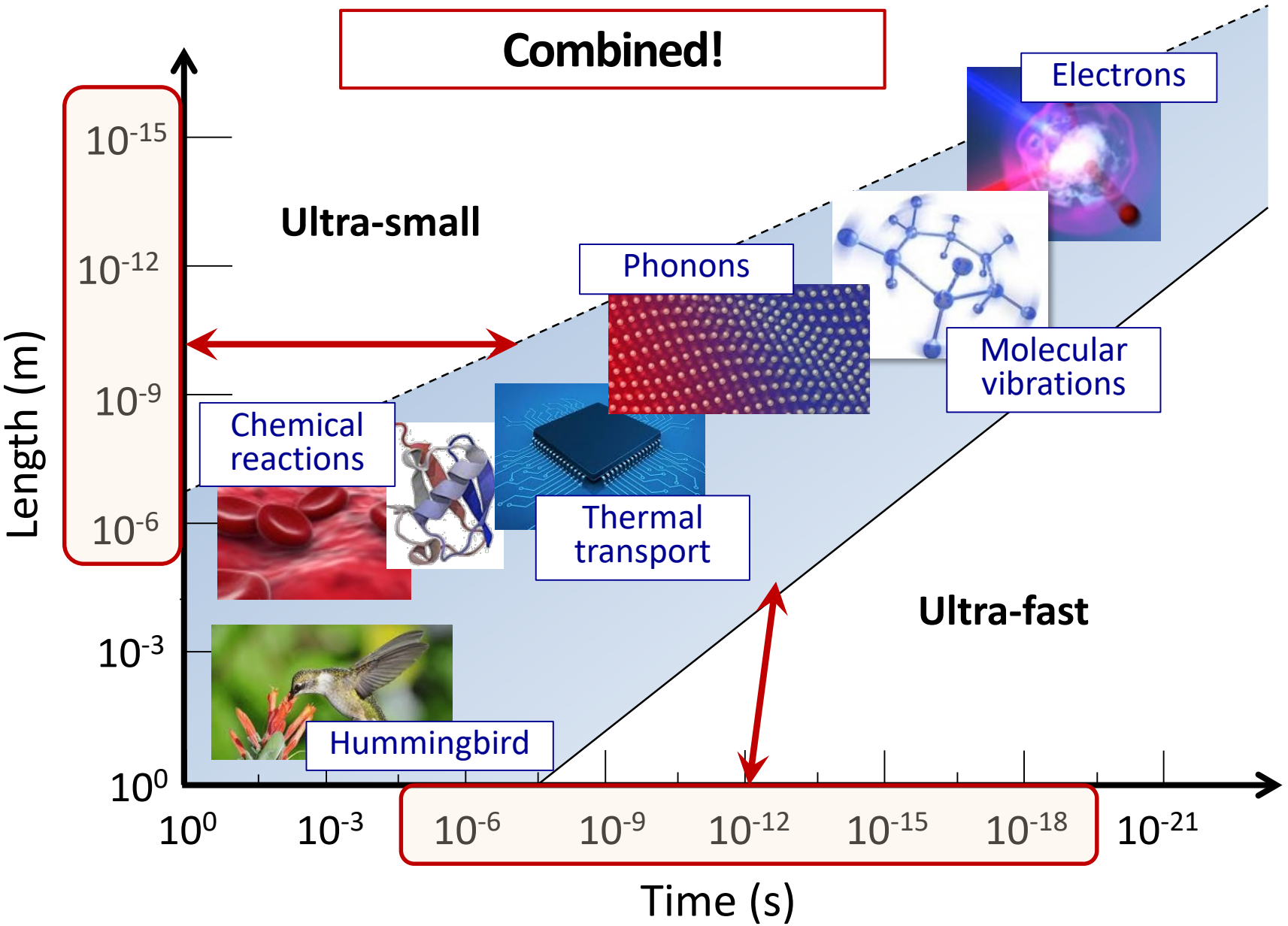
Renewable energy



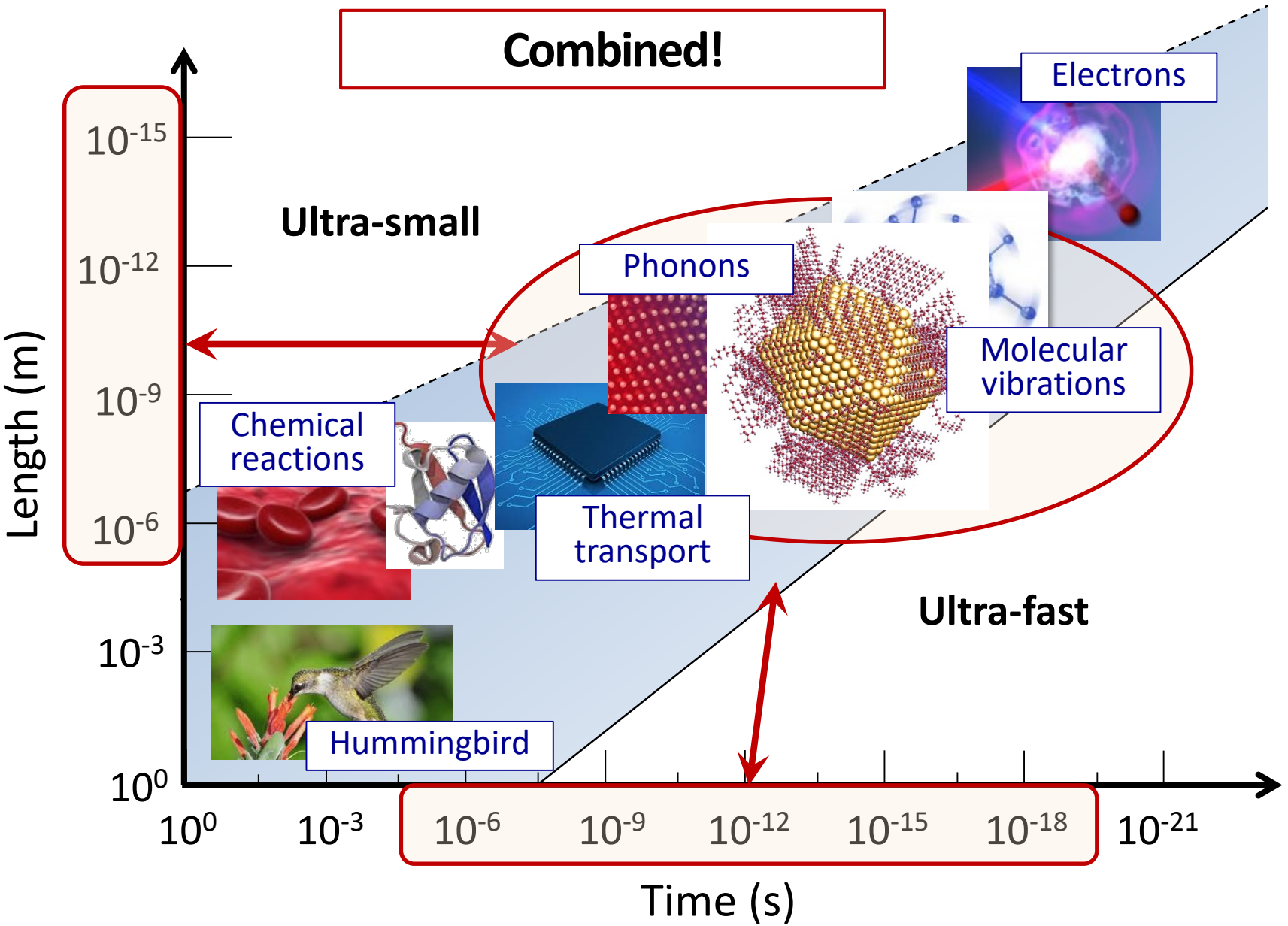
Communication → data storage & security

We need **new** characterization tools!

Measuring functional response



Measuring functional response

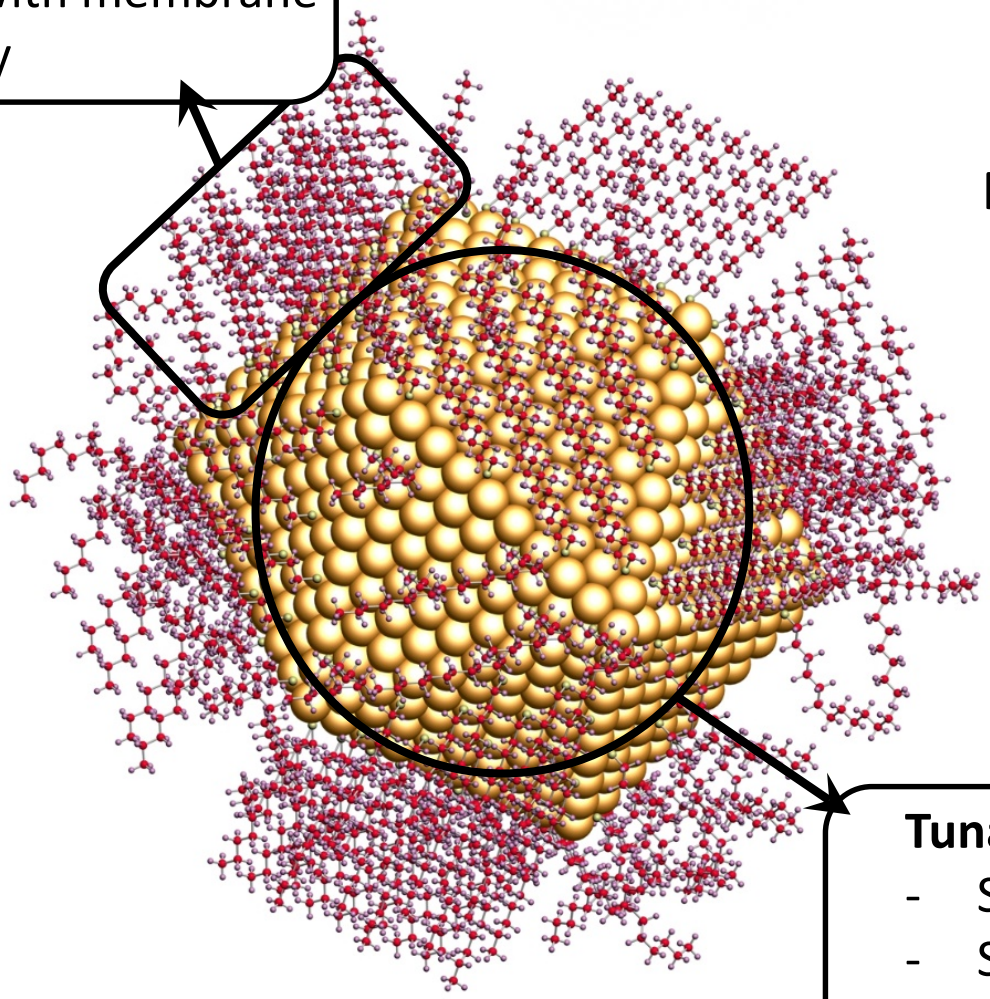


Building blocks...

Tunable:
- Chemistry
- Interaction with membrane
- Drug delivery

10^{-15}s

Functional response triggered by light

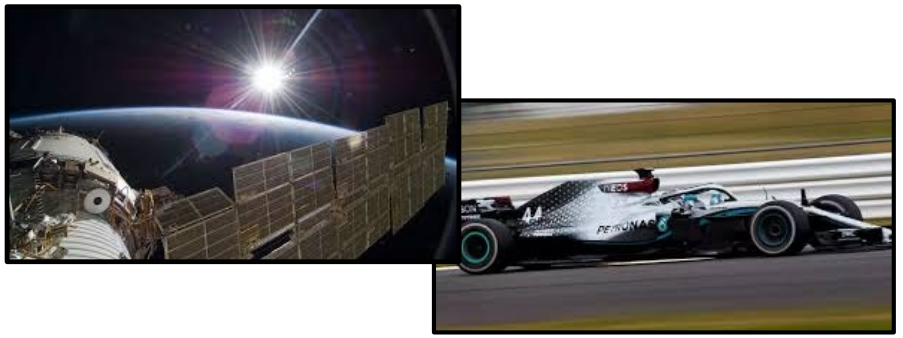


2-100 nm

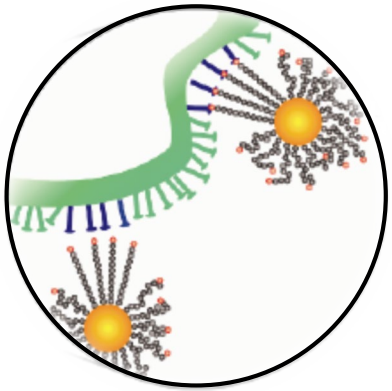
Tunable:
- Shape
- Size
- Composition

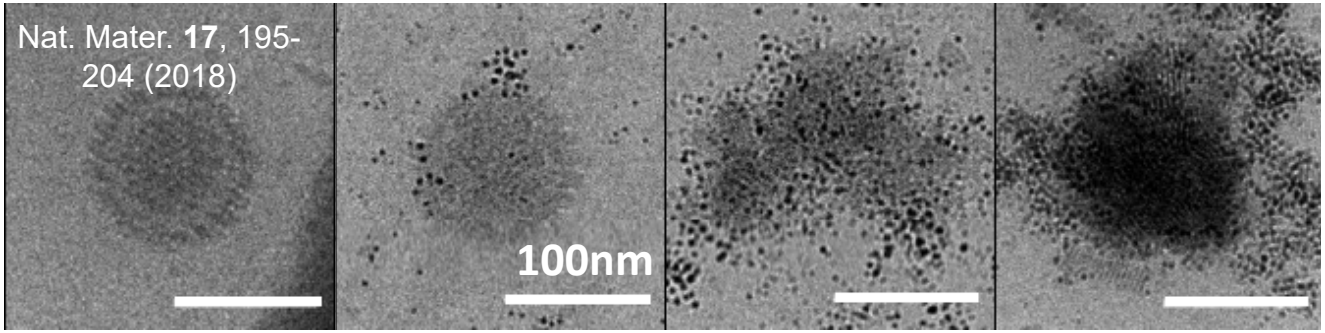
...in new functional nanomaterials

LEDs and photovoltaics
Suppression of trap-assisted non radiative-recombination

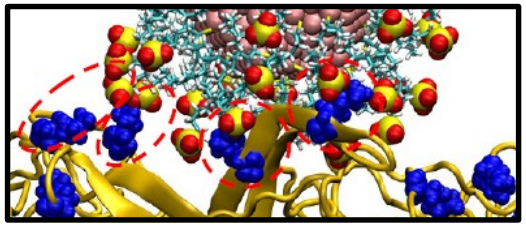


3Dynamics tech
Higher thermal load coating–
automotive, aerospace





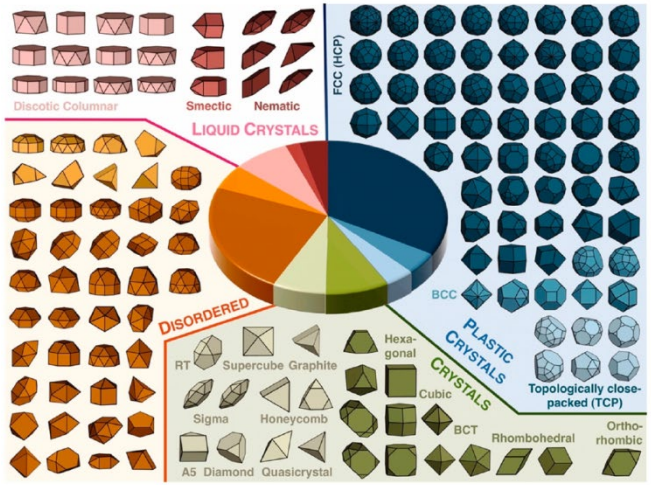
Cryo TEM

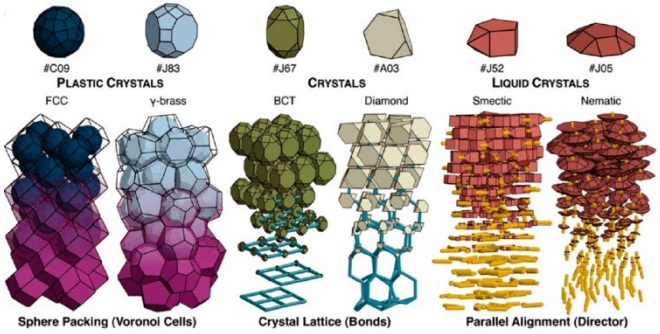


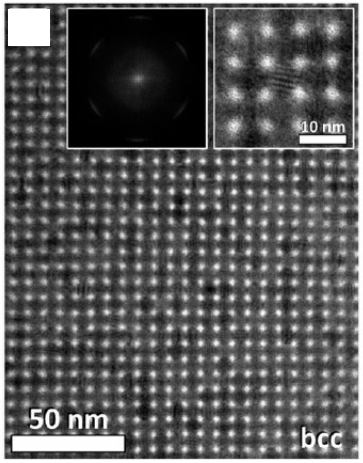
Extracellular inhibition, photostimulation
Theranostics, diagnostics

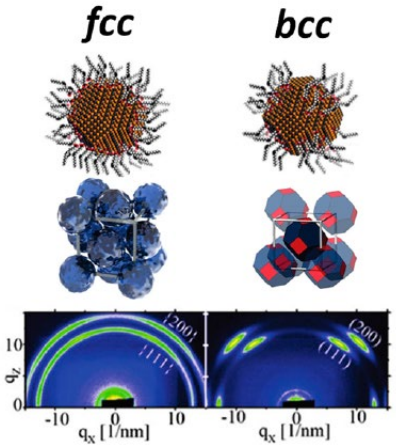
Structure-property relations

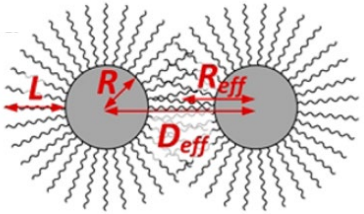
- **Electronic and optoelectronic applications:**
  - **Active element**: macroscopic arrays of **nanoparticles**
  - **Tailor size, shape, composition** for fine-tuning of material **physical properties**
    Charge-carrier dynamics, thermal transport, stiffness, long-term stability […]
  - **Functionalized** nanoparticles: ligand length and order









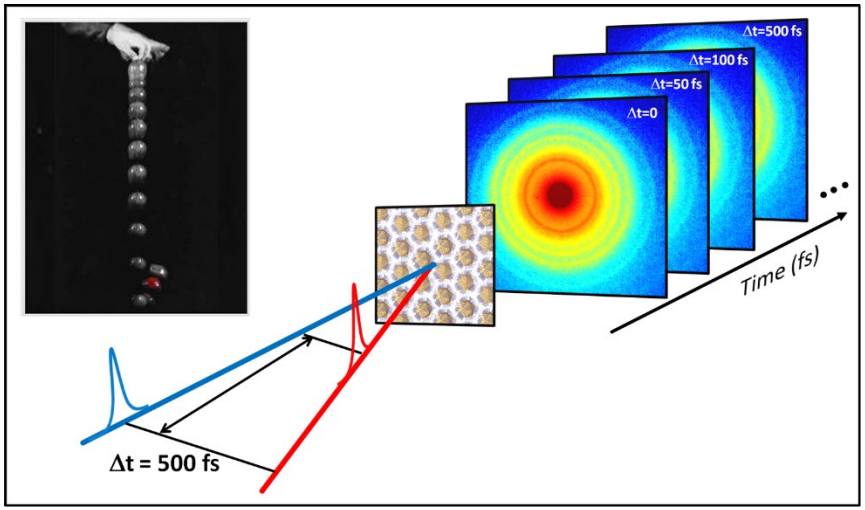


P. F. Damasceno, M. Engel, S. C. Glotzer, Science **337**, 453–457 (2012)
J. J. Choi, *et al.* J. Am. Chem. Soc. **133**, 3131–3138 (2011)
M. A. Boles, D. V. Talapin, J. Am. Chem. Soc. **137**, 4494–4502 (2015)

Ultrafast methods

Ultrafast lasers

- Pulse trains
- 10^{-15}s pulse duration
- µm to nm wavelength



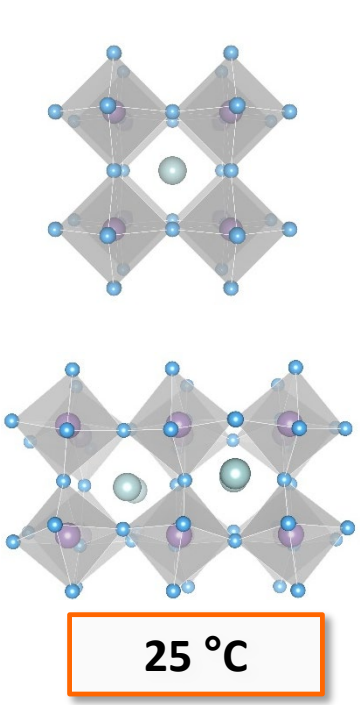
Pump pulse

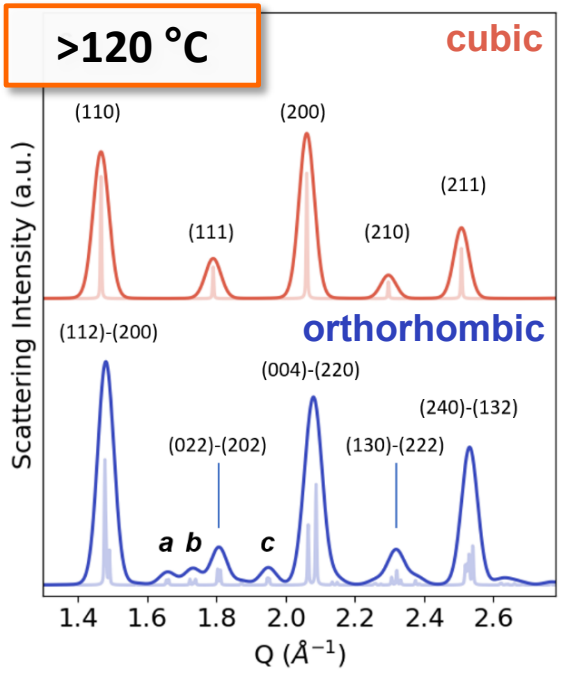
- Initiates dynamics
- Reference point in time

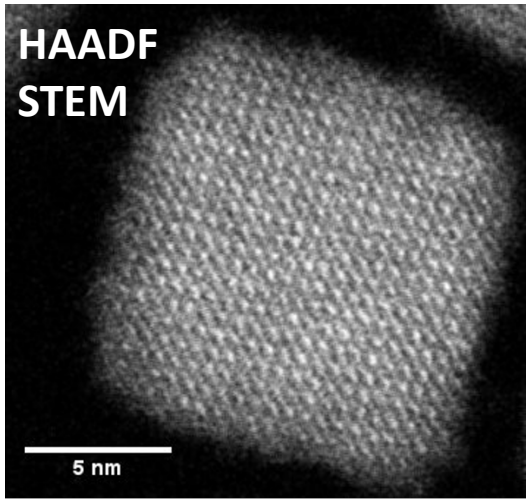
Probe pulse

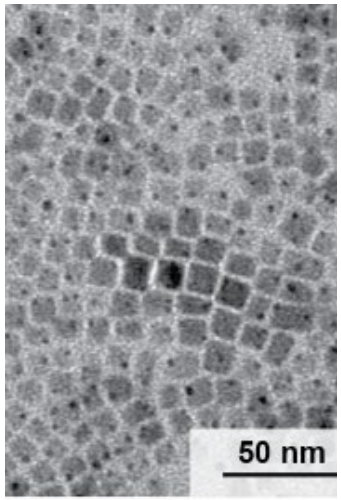
- Images and spectra show electronic/structural changes

Light-induced response in $CsPbBr_3$









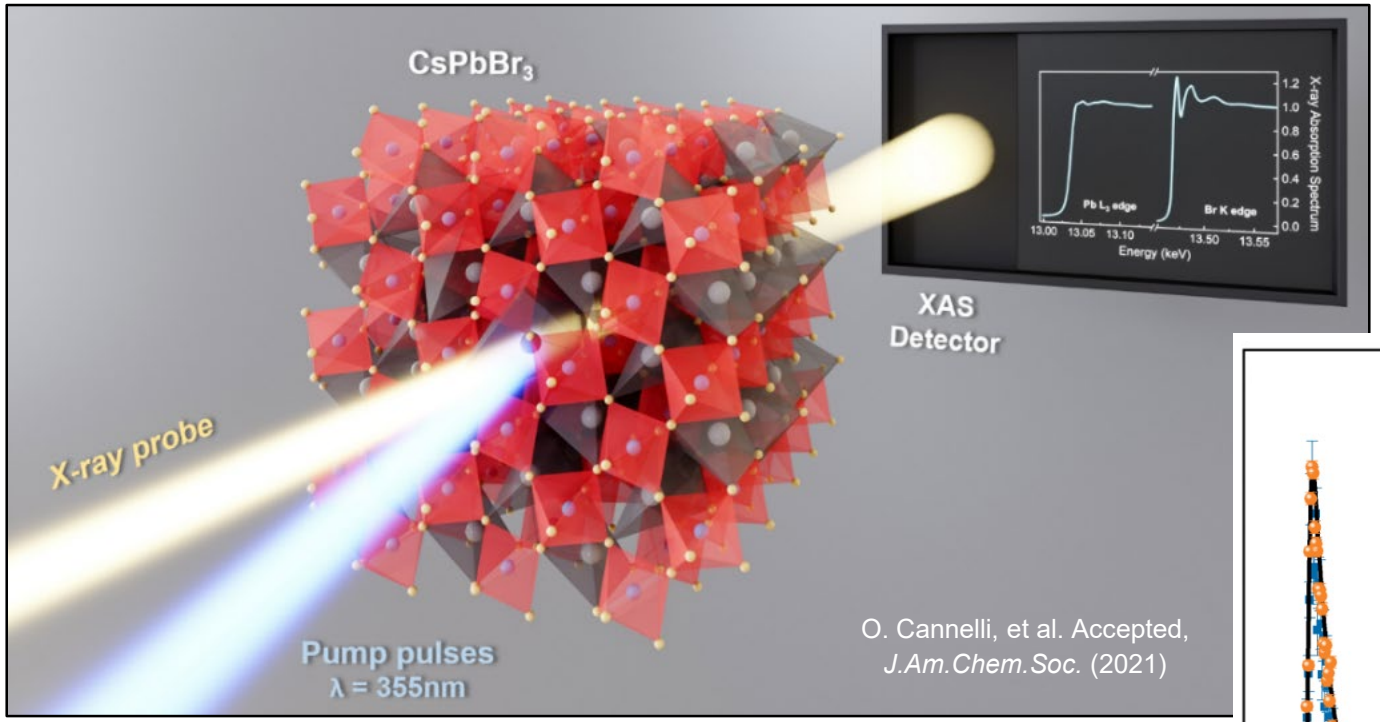
Perovskites:

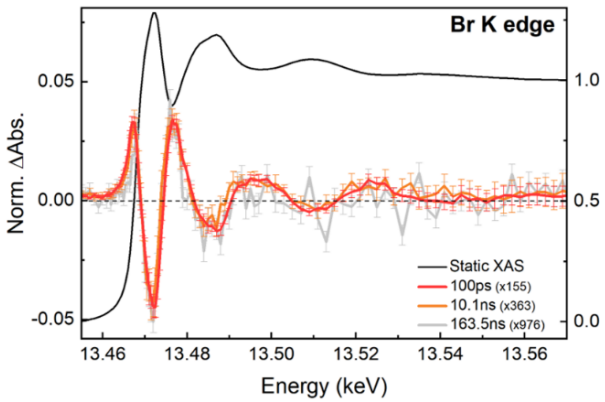
- Long carrier lifetime & diffusion lengths
- Pb-Br framework flexibility

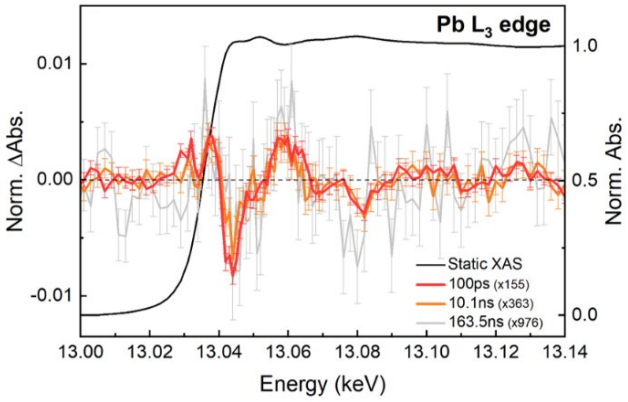
Wishlist for realistic applications:

- Understanding of **the interaction between charge carriers and the polar lattice** in out-of-equilibrium conditions
- Comprehensive **atomistic picture of light & thermal activations**

TR-XAS: Br K and Pb L_3 edges







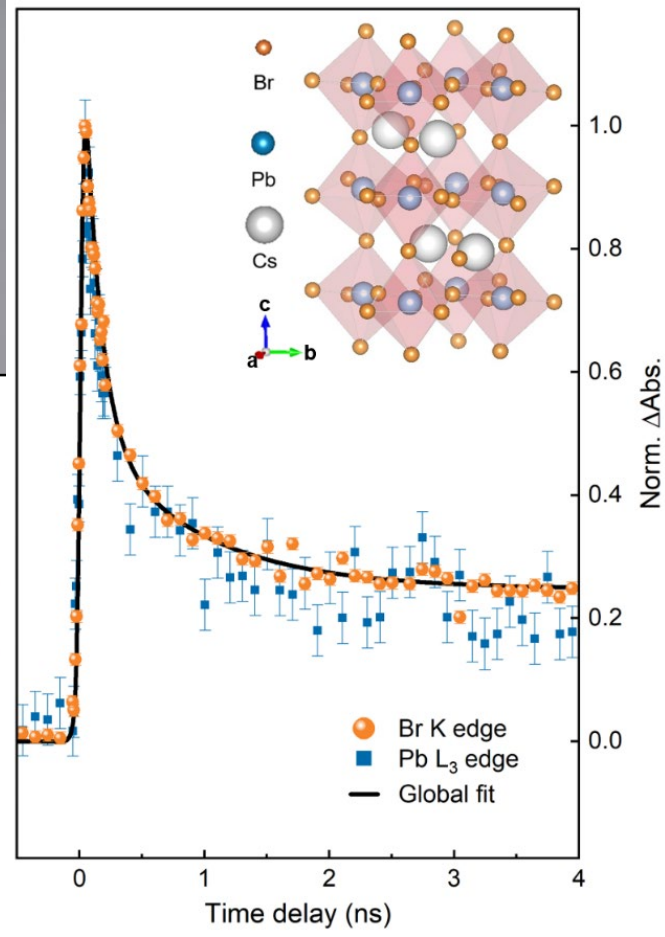
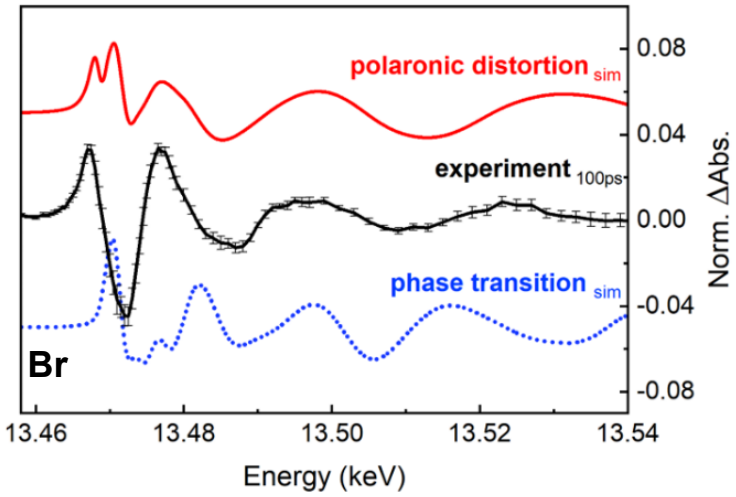


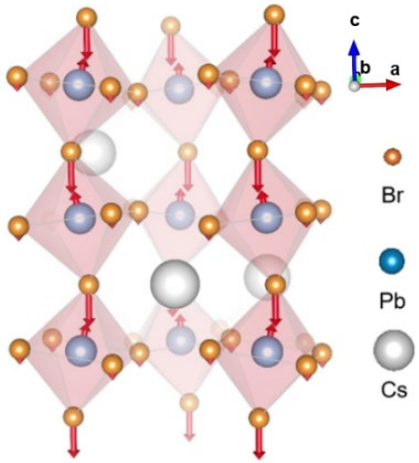
Photo-induced polaronic distortions

XANES spectrum: local reticular distortions



***ab-initio*, Core-hole final state effects**

LO phonon 18meV

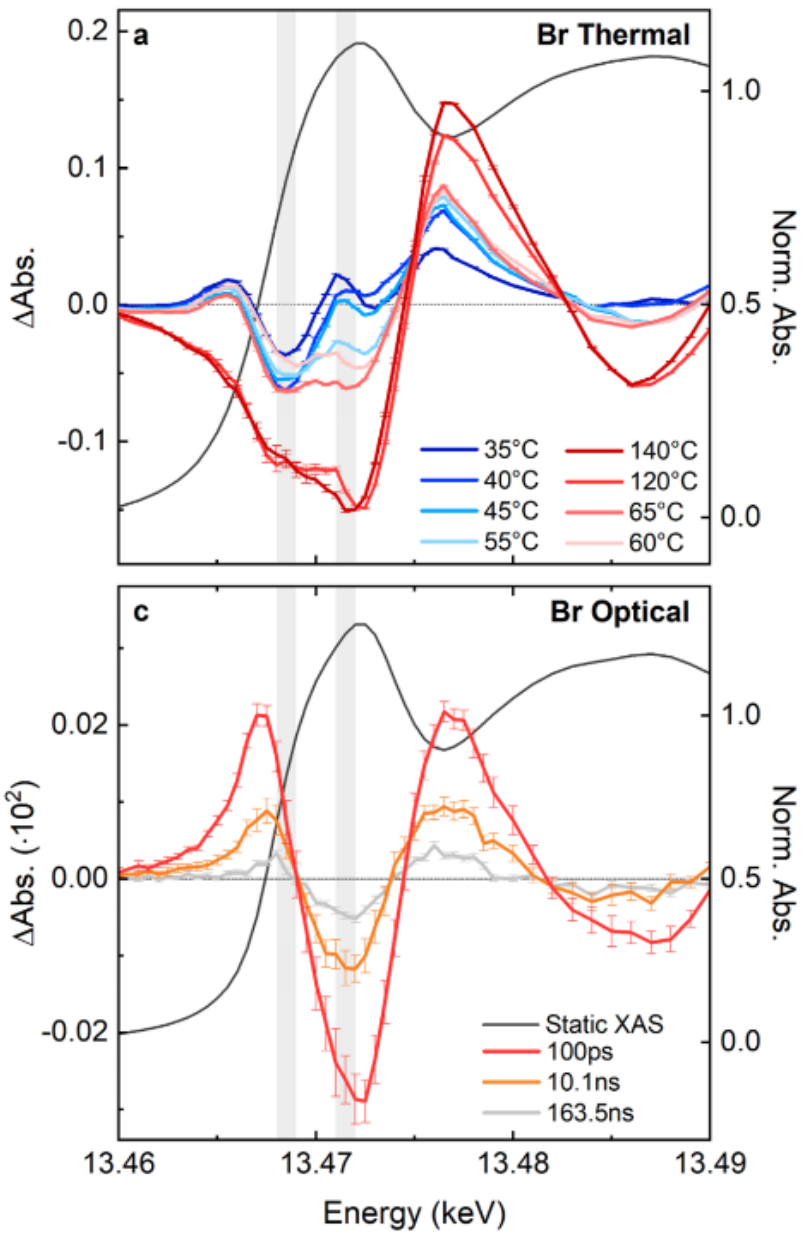


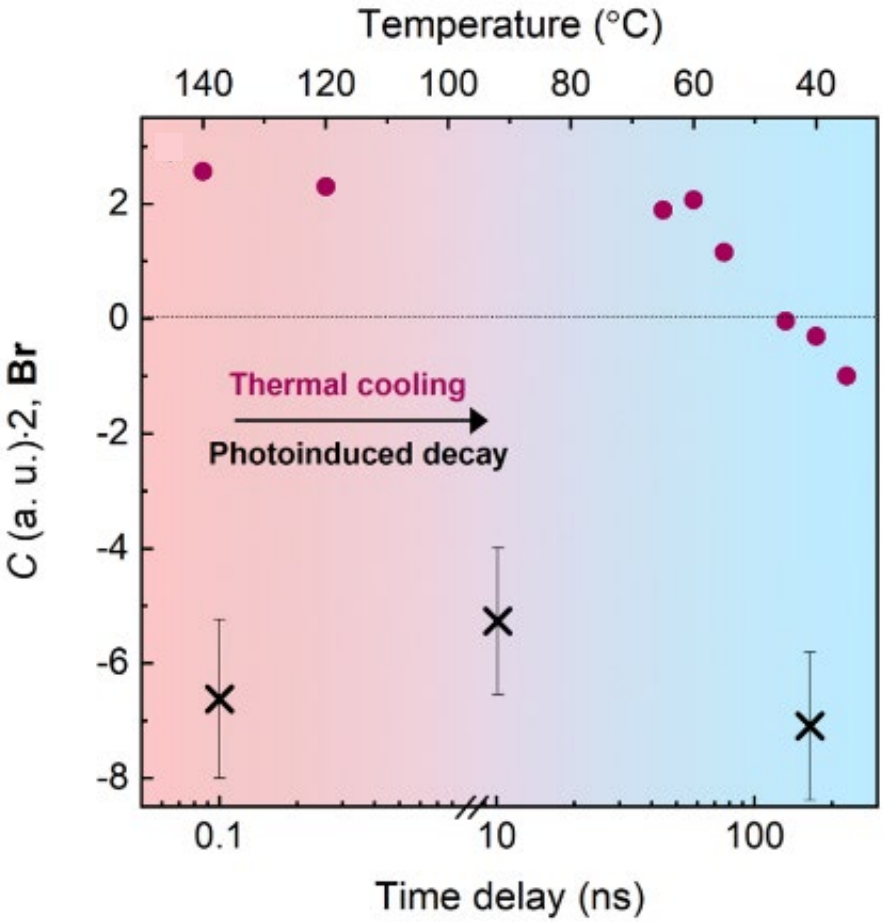
M. Puppin *et al.*, Phys. Rev. Lett. **124**, 206402 (2020

Main results:

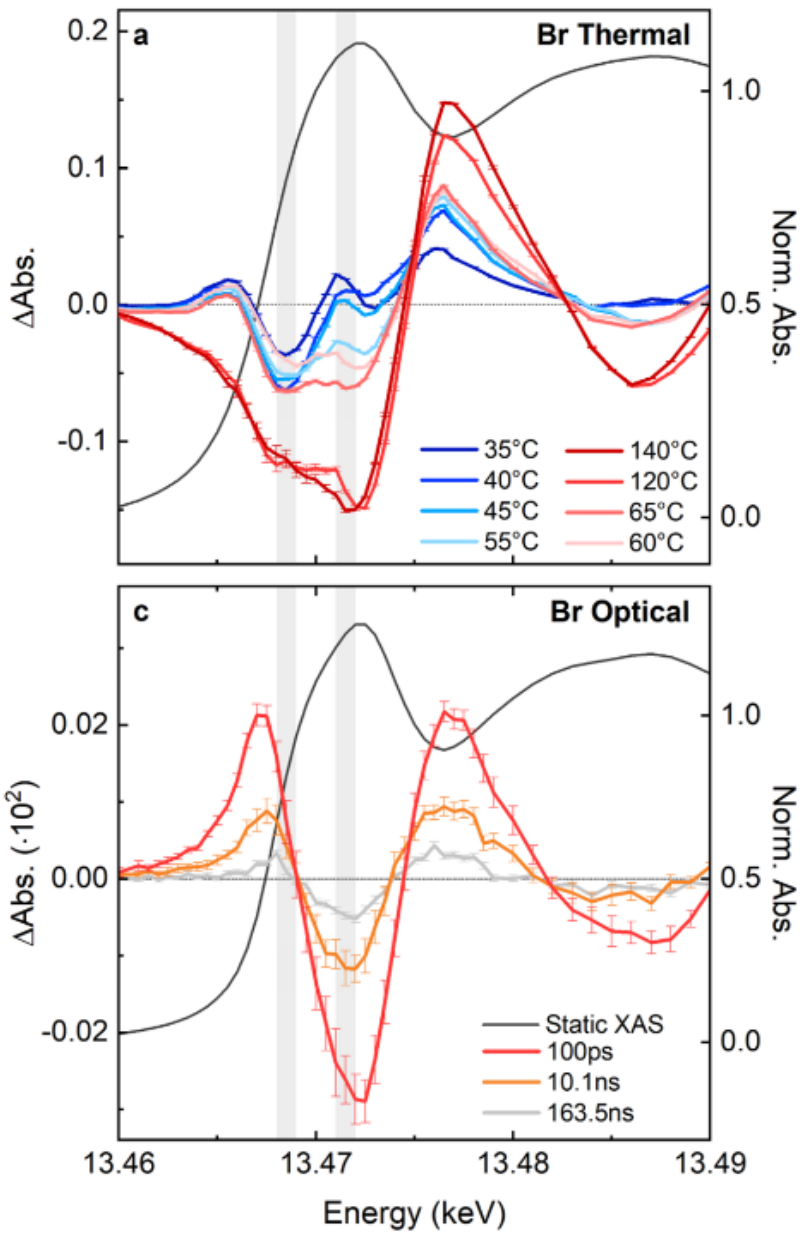
- **Charge-carrier recombination unlocks polaronic structural distortions**
- Specific **activation of a longitudinal optical phonon mode at 18 meV *via* electron-phonon coupling** (**RED**)
- No interplay of light-induced orthorhombic-cubic phase transitions (**BLUE**)
- Auger recombination τ_1=120±20 ps, Radiative recombination τ_2=900±300 ps

Ruling-out thermal effects in photo-induced activation





Ruling-out thermal effects in photo-induced activation



Thermal fluctuations & phonon anharmonicity

- Co-existing orthorhombic and cubic phases of $CsPbBr_3$ in single particles at room T *and high T*

Systems too complex to be modelled from first principles *with* core-hole:

- Direct visualization of heterogeneity
- Straightforward visualization of the sample

O. Cannelli, et al., *In preparation.* (2021)
Y. Yu et al., Nano Lett. 16, 7530-7535 (2016)

Ultrafast/high-resolution imaging

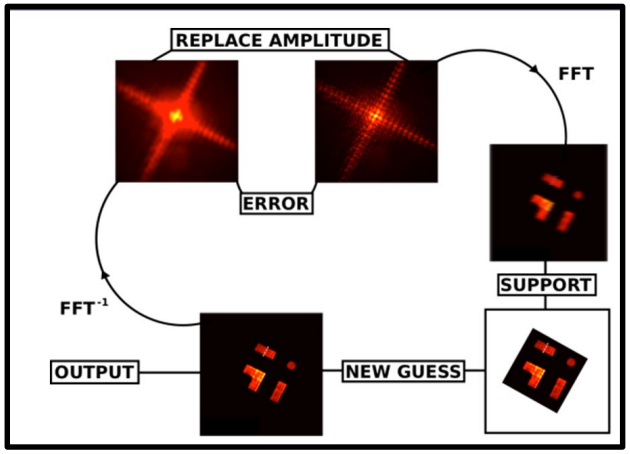
- **Direct-space imaging**

Microscope objective lens

Image formation

- **Imaging with phase retrieval**

Computer



Phase Retrieval algorithm

Miao et al., Nature, **400**, 342 (1999)
Fienup, Optics Letters **3**, 27 (1978)

Chapman et al., Nature Photonics, **4**, 833 (2010)
Chao et al., Nature **435,** 03719 (2005)

Rodenburg et al. Phys. Rev. Lett. **98** ,034801 (2007)
Seaberg et al., Optics Express **19**, 22470 (2010)
Miao et al., Science **348**, 530 (2015)

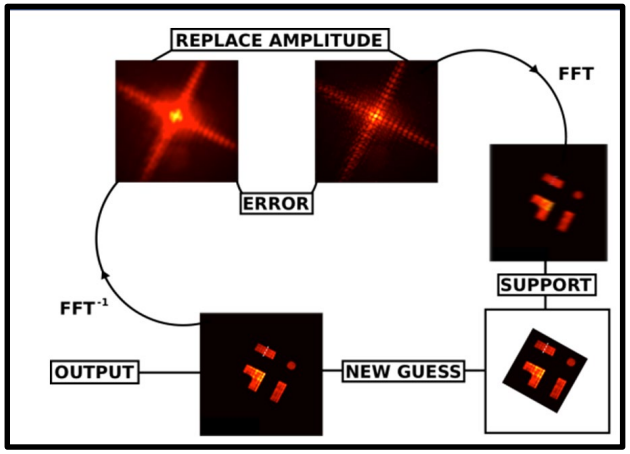
Ultrafast/high-resolution imaging

Electrons: Diffractive imaging? Holography? Limited by coherence and flux – maximum likelihood

X-rays: Coherent diffractive imaging, holography – full-field

- **Imaging with phase retrieval**

Computer



Phase Retrieval algorithm

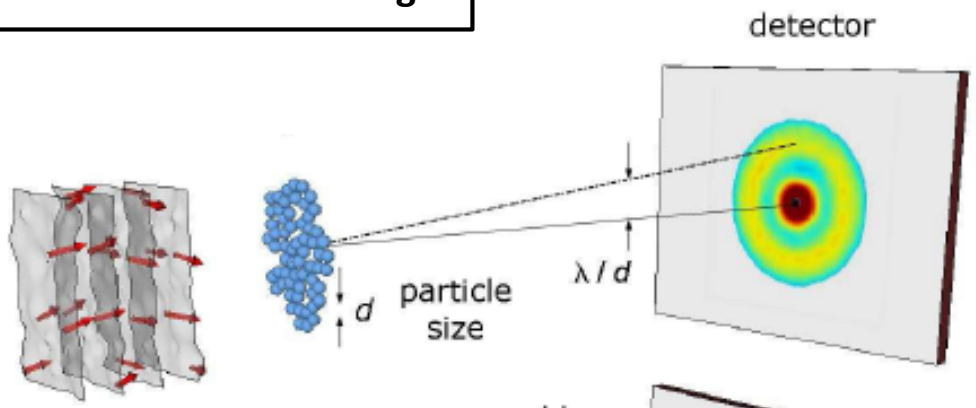
Miao et al., Nature, **400**, 342 (1999)
Fienup, Optics Letters **3**, 27 (1978)

Chapman et al., Nature Photonics, **4**, 833 (2010)
Chao et al., Nature **435,** 03719 (2005)

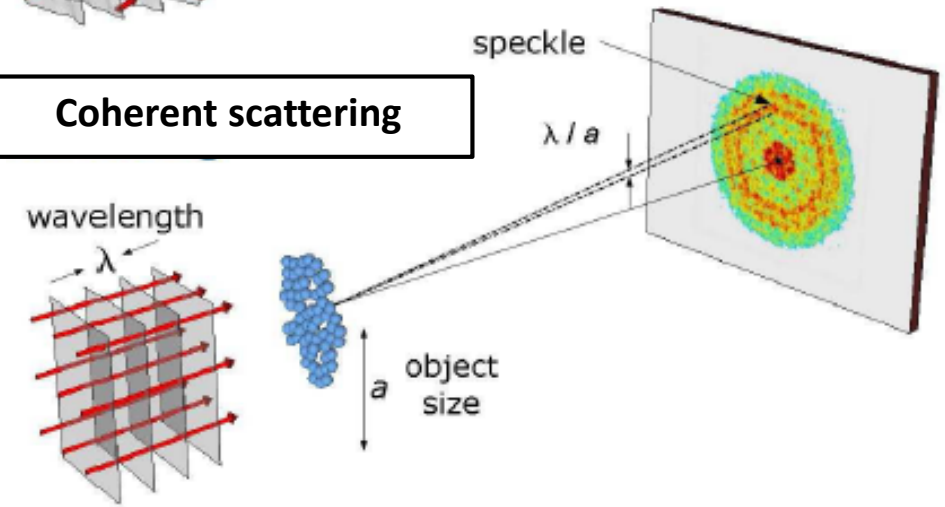
Rodenburg et al. Phys. Rev. Lett. **98** ,034801 (2007)
Seaberg et al., Optics Express **19**, 22470 (2010)
Miao et al., Science **348**, 530 (2015)

Probing speckles with electrons

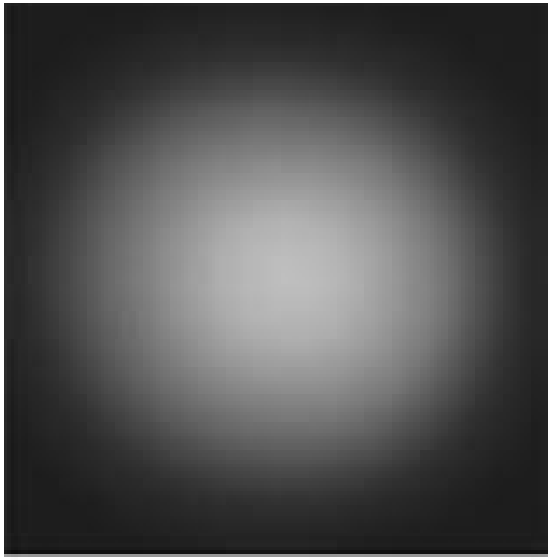
Incoherent scattering

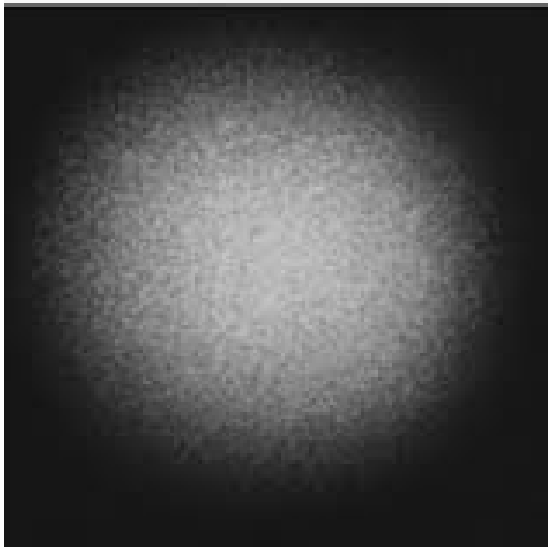


Coherent scattering



Symmetry retrieval from speckle analysis

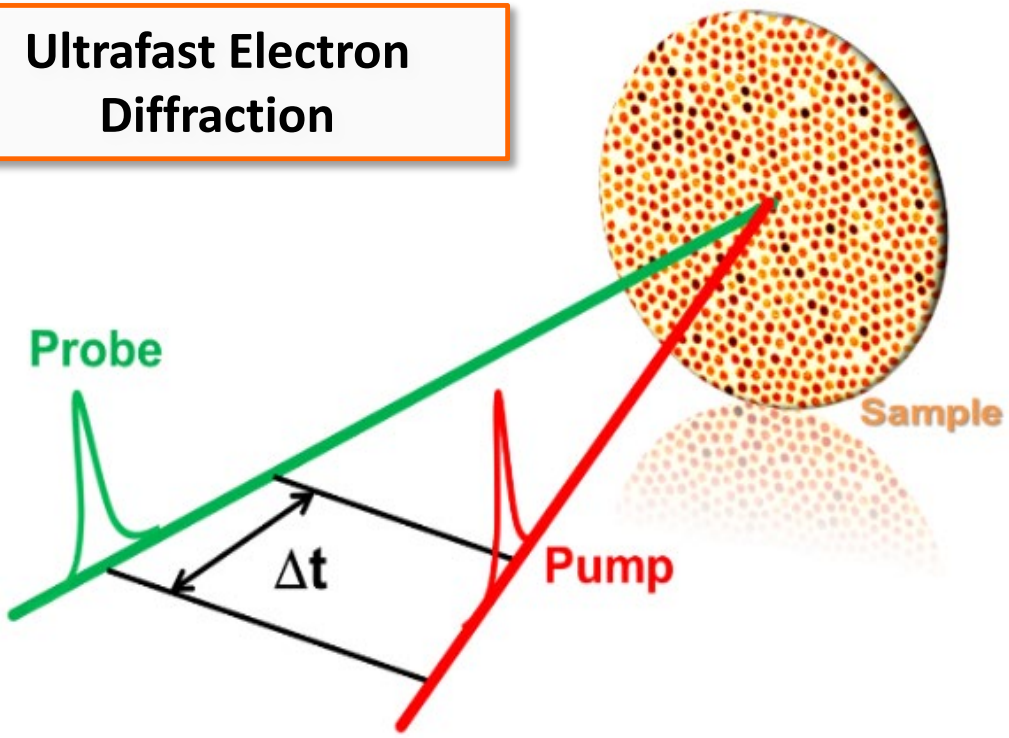


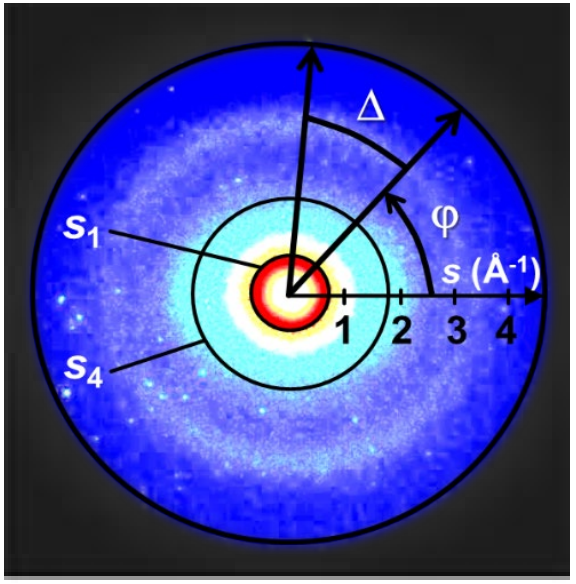


Kam, Z. Macromolecules 10, 927–934 (1977)
Altarelli, M., Kurta, R. P. & Vartanyants, I. A.. Phys. Rev. B 82, 104207 (2010).

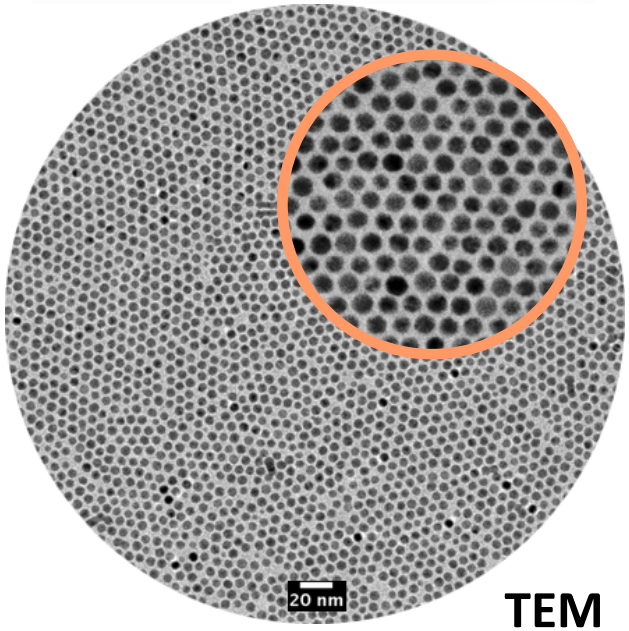
Probing speckles with electrons

Ultrafast Electron Diffraction





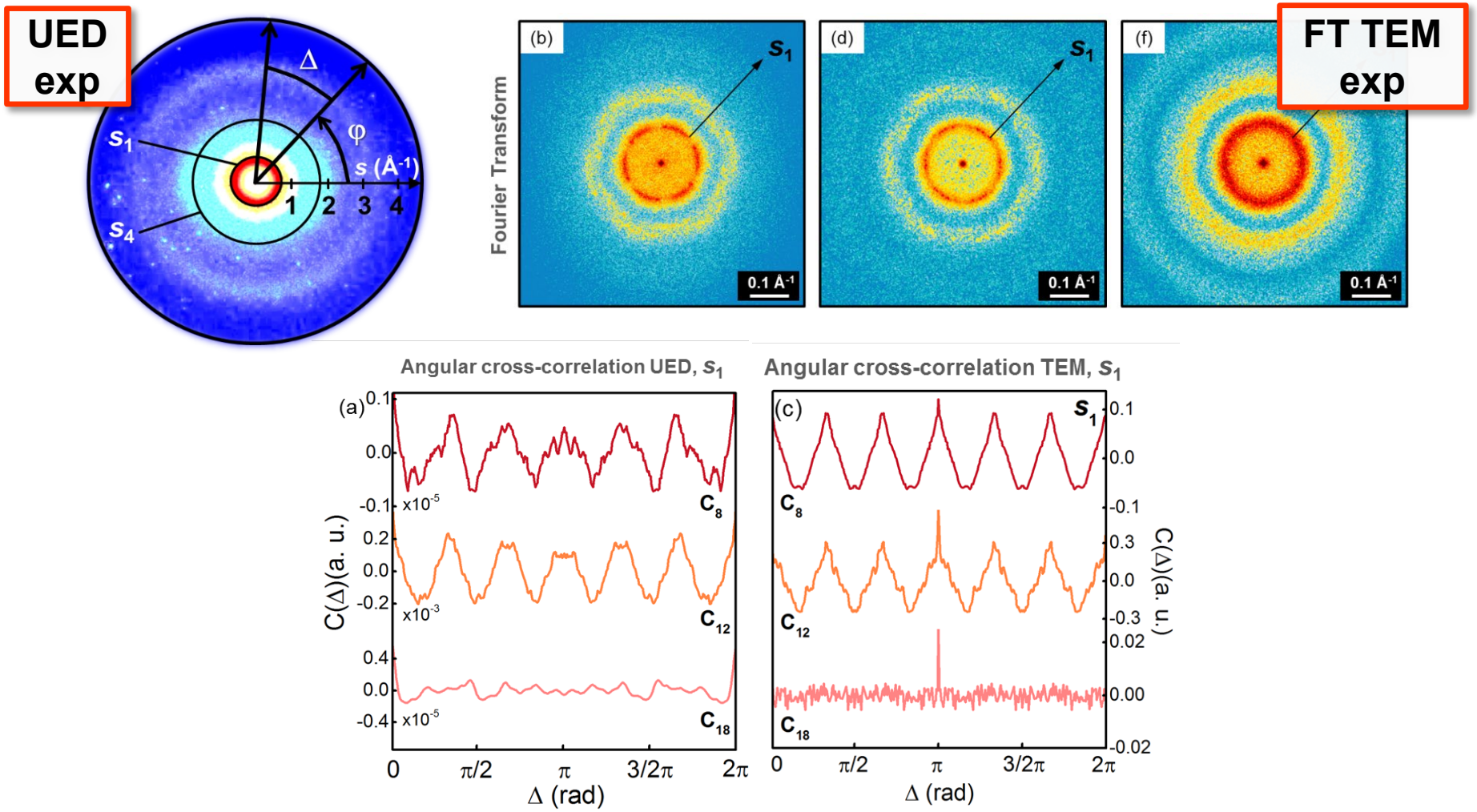
$$C_s(\Delta) = \frac{\left\langle I(s,\phi)I(s,\phi+\Delta)\right\rangle_\phi - \left\langle I(s,\phi)\right\rangle_\phi^2}{\left\langle I(s,\phi)\right\rangle_\phi^2}$$



TEM

G. F. Mancini *et al.*, Nucl. Instrum. Methods Phys. Res. A **691**, 113 (2012)
G. F. Mancini et al., NanoLett. **16** 2705 (2016)

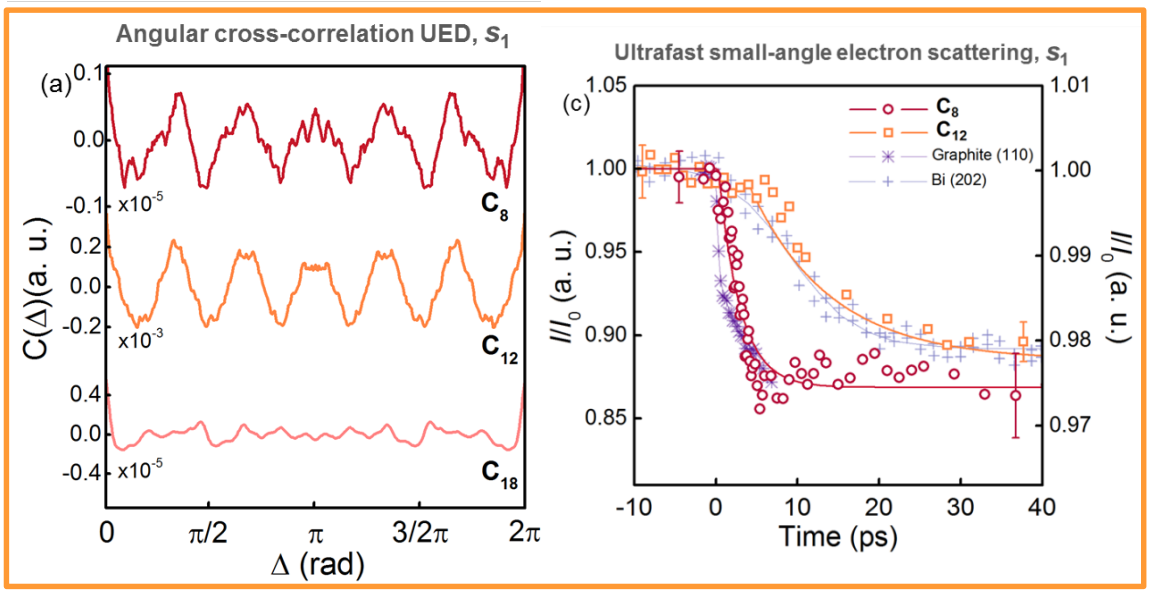
Diffraction Imaging: mechanical stiffness in Au-NPs

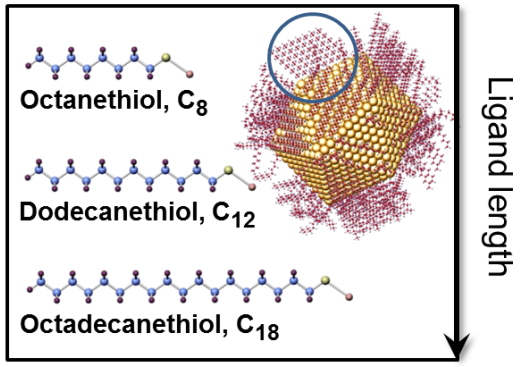


Beyond established powder diffraction data analysis:

- Local **order/disorder** correlations, spatial organization & photodynamics
- Ligands (S,C,H) ordering & Au core dynamics in supracrystal - in the same experiment

Ligand length dependent e⁻-ph coupling

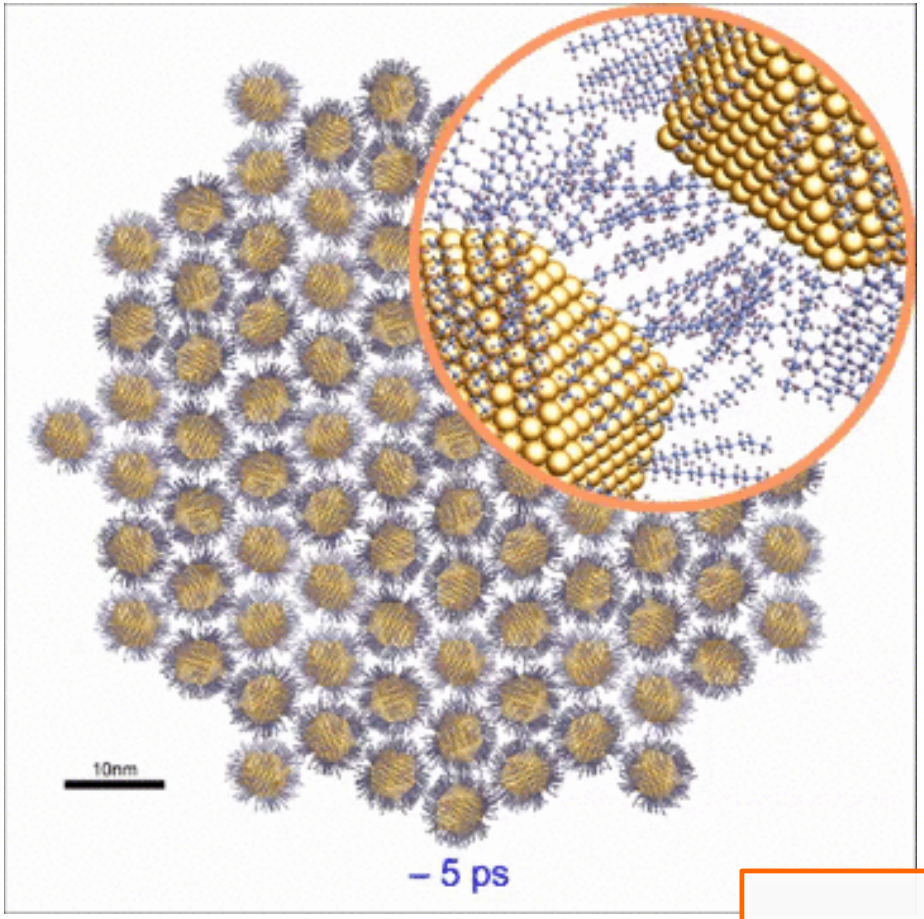




G. F. Mancini et al., Struct. Dyn. **6**, 024304 (2019)

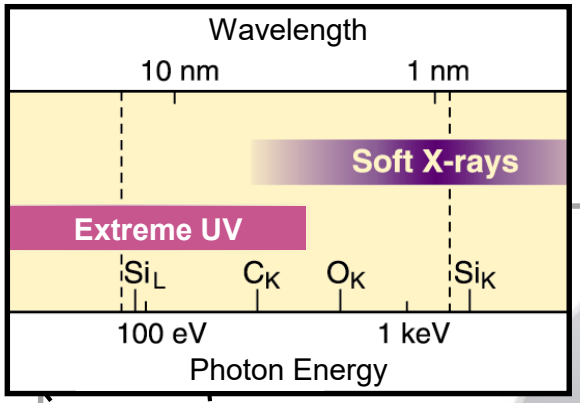
- C8: τ = 2.6 ± 0.3 ps. C12: τ = 12.1 ± 0.9 ps
- **Intensity suppression**: energy transfer between the electronic excitation and the structural degrees of freedom of each supracrystal.
- C8 supracrystal. **Interdigitation: efficient channel for transferring energy** between the initial electronic excitation to structural motions of the NPs.
- **Local stiffness** in a dense **supramolecular assembly** can be created by **Van der Waals** interactions up to a level **comparable** to **systems** characterized by **covalent bonding**.

The nanoscale *quasi*-movie

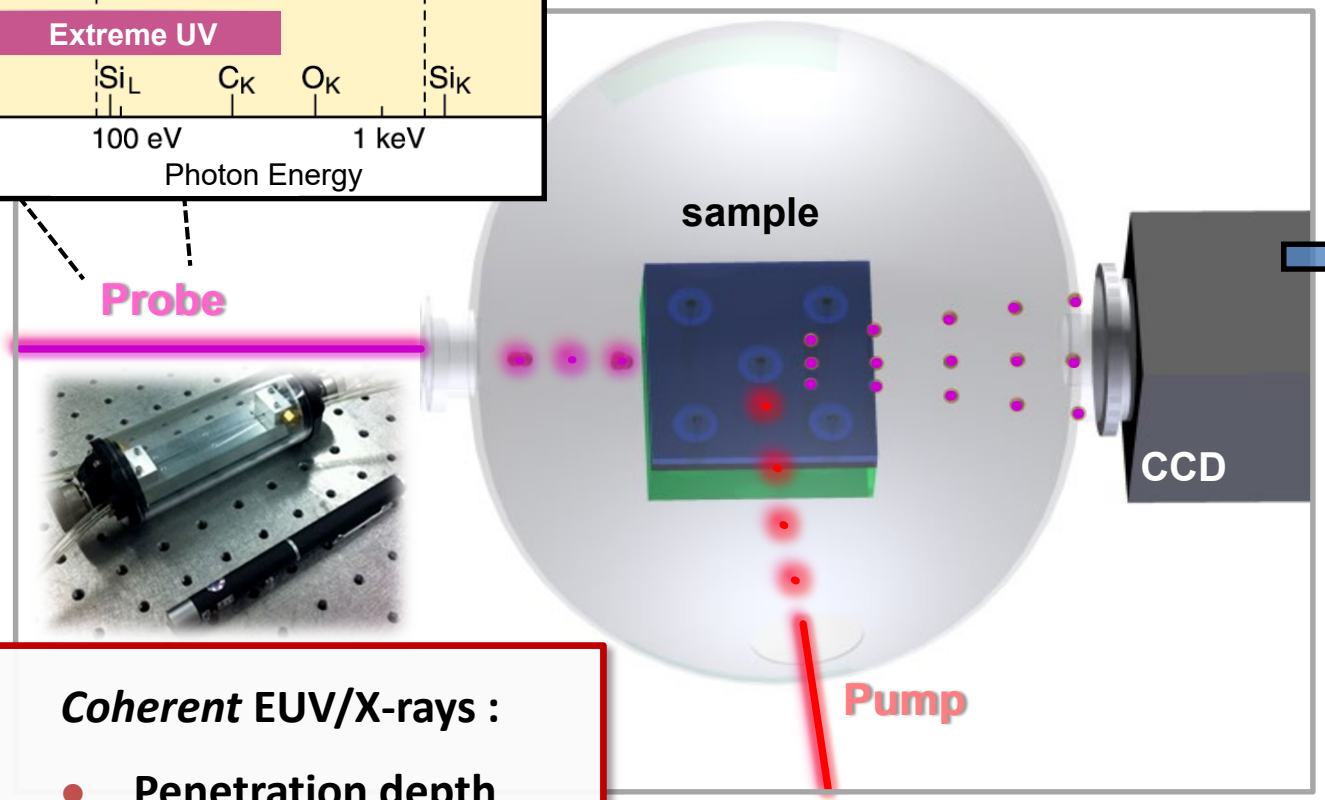


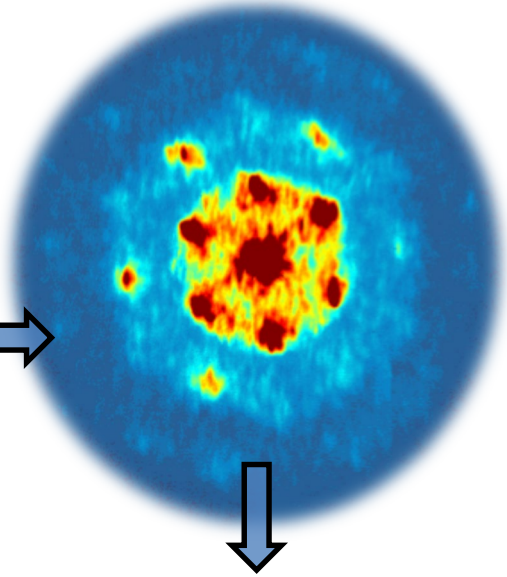
Optically-induced ligand annealing & grain separation

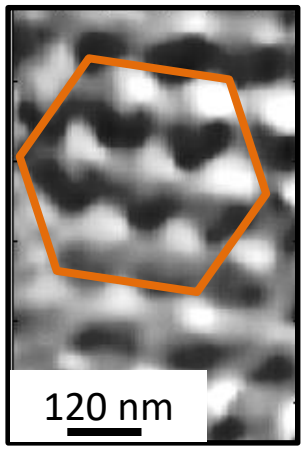
Tabletop microscopy from High-Harmonic Generation



Quantitative : number of layers, oxidation and diffusion processes





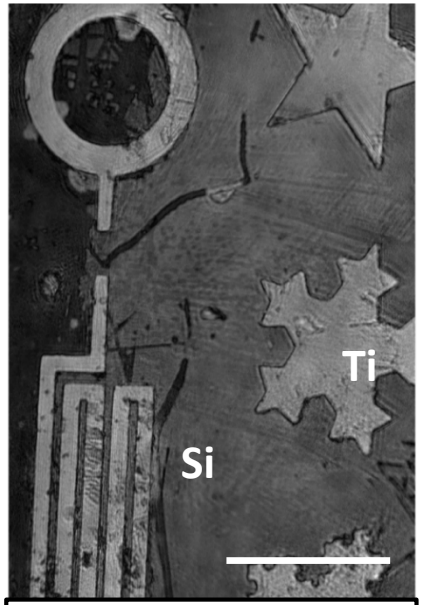


Coherent **EUV/X-rays :**

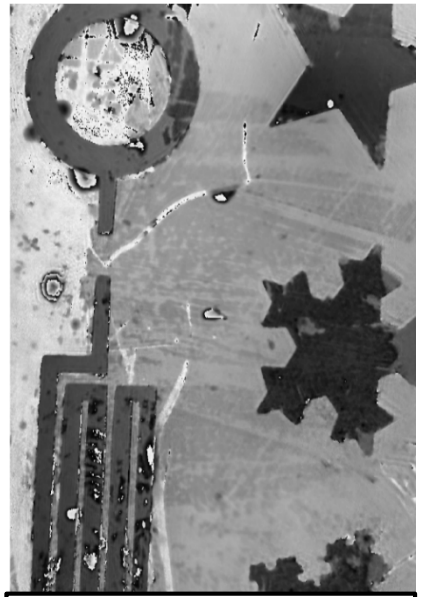
- **Penetration depth**
- **Capture dynamics** relevant to function
- High **coherence**

G. F. Mancini, *et al.*, Opt. Express **26**, 11393–11406 (2018),
Nature Photonics **11**, 259-263 (2017)
E. Shanblatt *et al., Nano Lett.* **16**, 5444–5450 (2016)

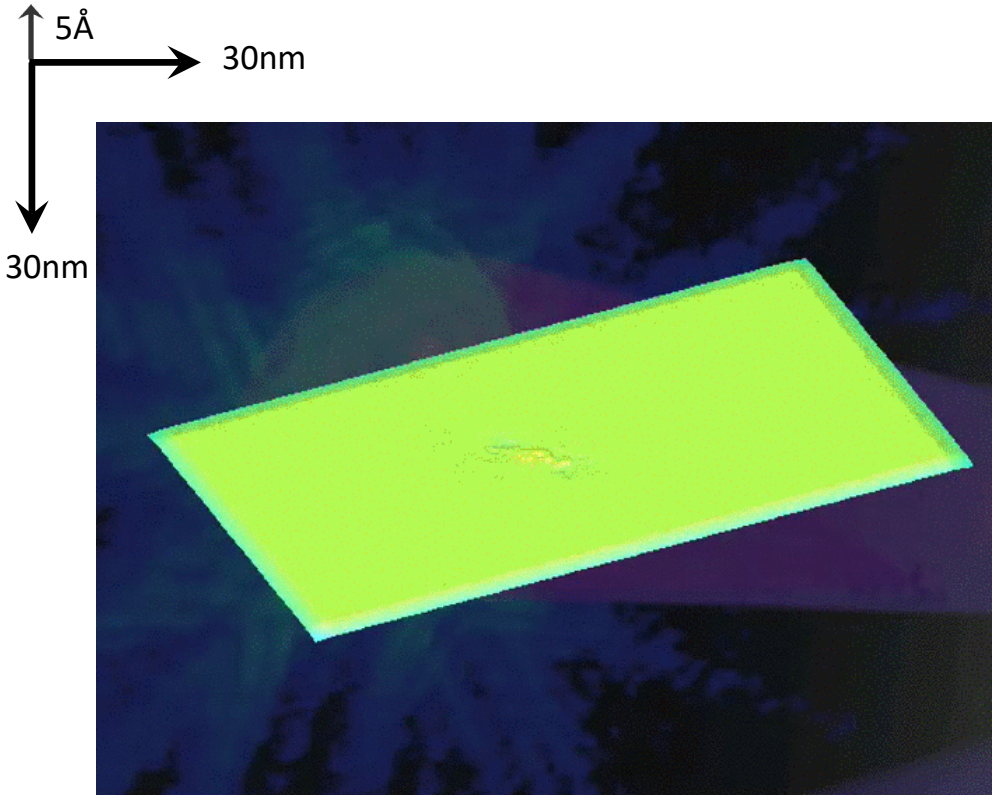
Ptychography with tabletop EUV light...

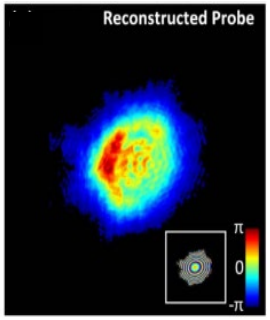


Amplitude:
Material composition



Phase:
Topography



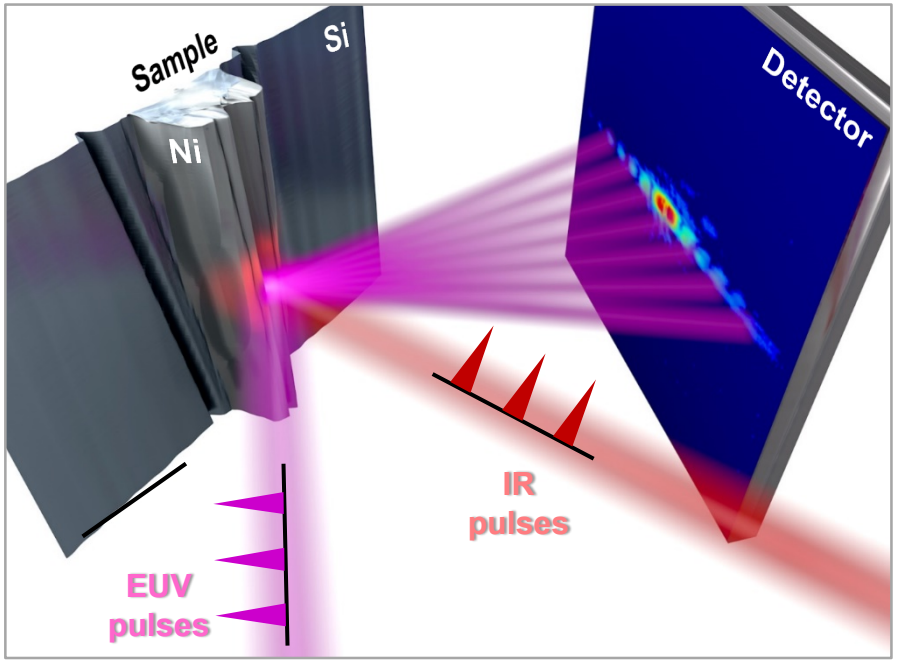


Separates **object** and **illumination**

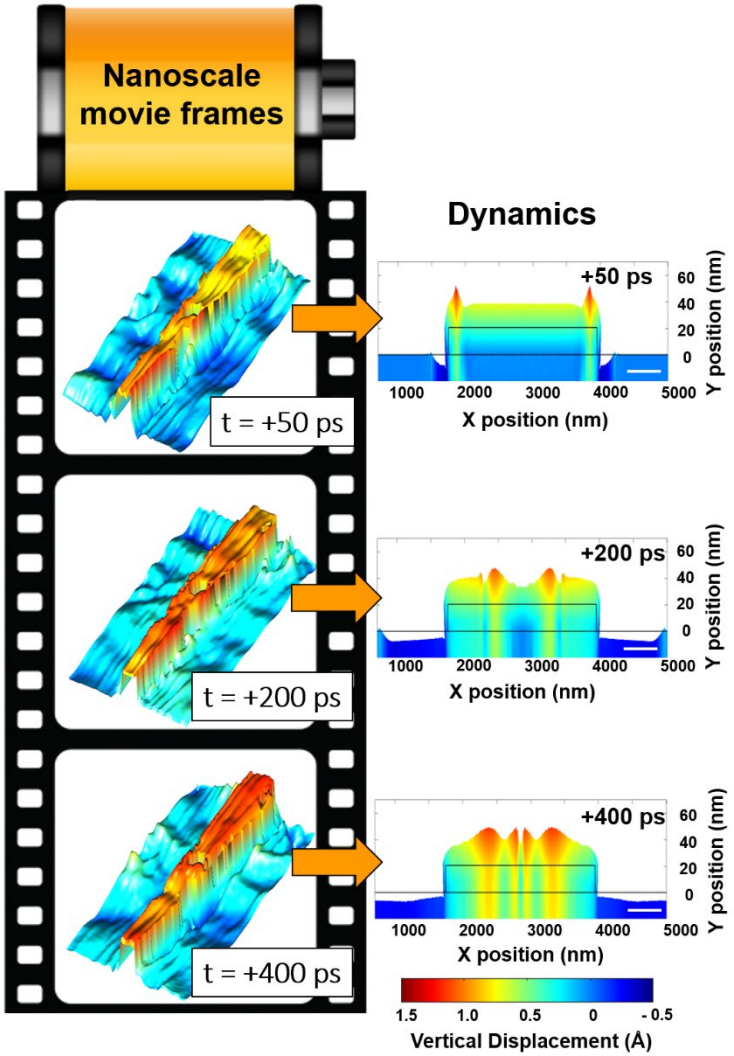
Zhang *et al.*, Ultramicroscopy **158**, 98 (2015)

In time...

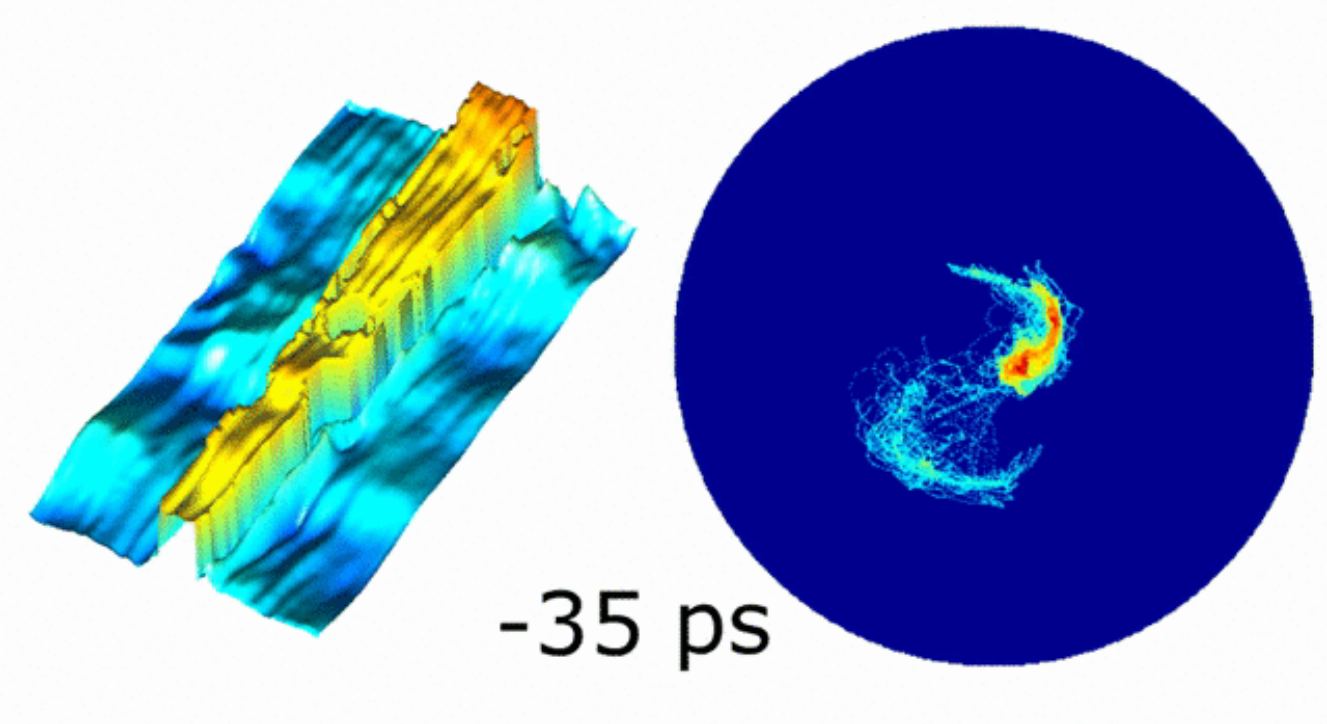
Snapshots of the 3D topology map upon impulsive excitation unravels waveguide dynamics & acoustic waves dispersion



Karl, Mancini, *et al.,* Sci. Adv. **4**, eaau4295 (2018)



The nanoscale movie



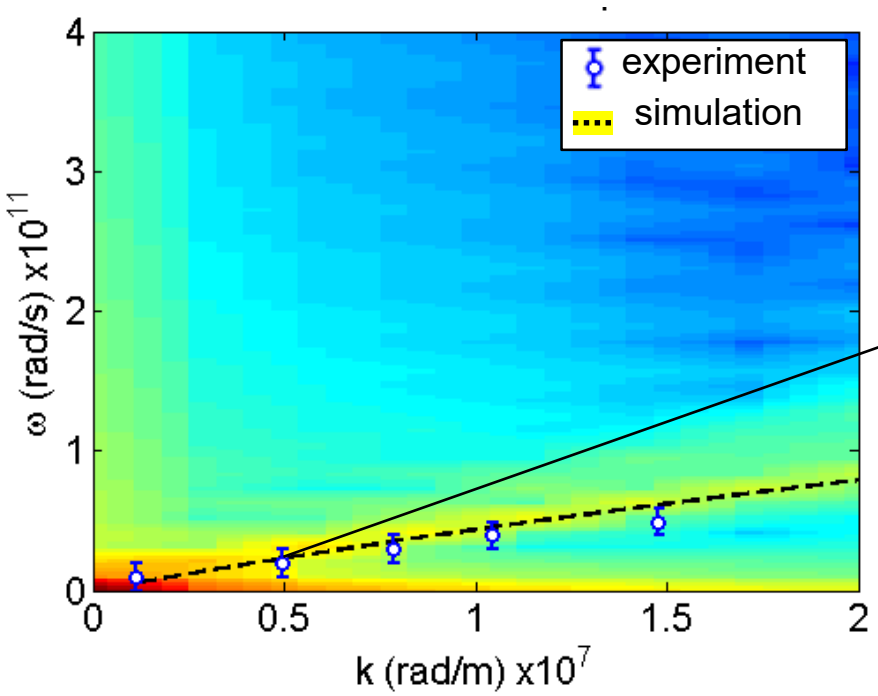
50ps

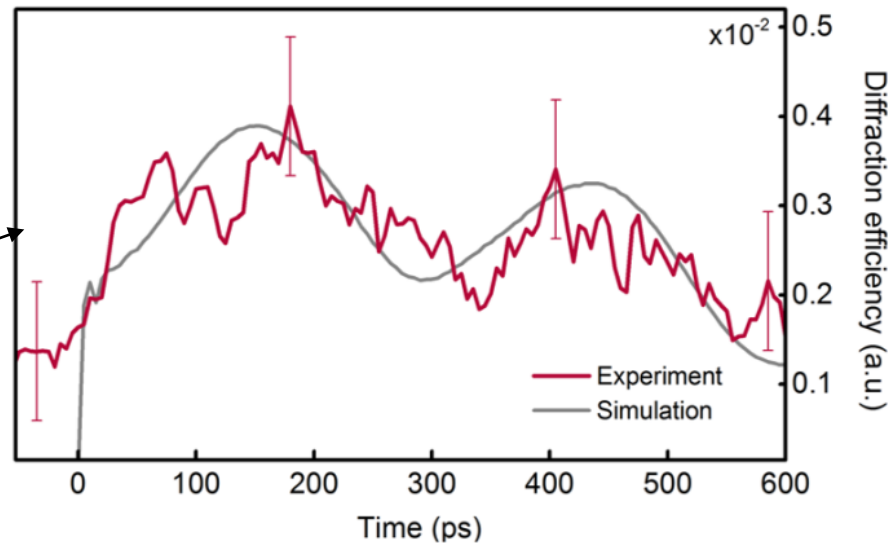
- **Impulsive expansion** at the edges of the nanostructure
- **Depression in the substrate** immediately adjacent to the nanostructure

400ps

- **Surface expansion** of the nanostructure progressively **propagates** from the edges towards the **center**

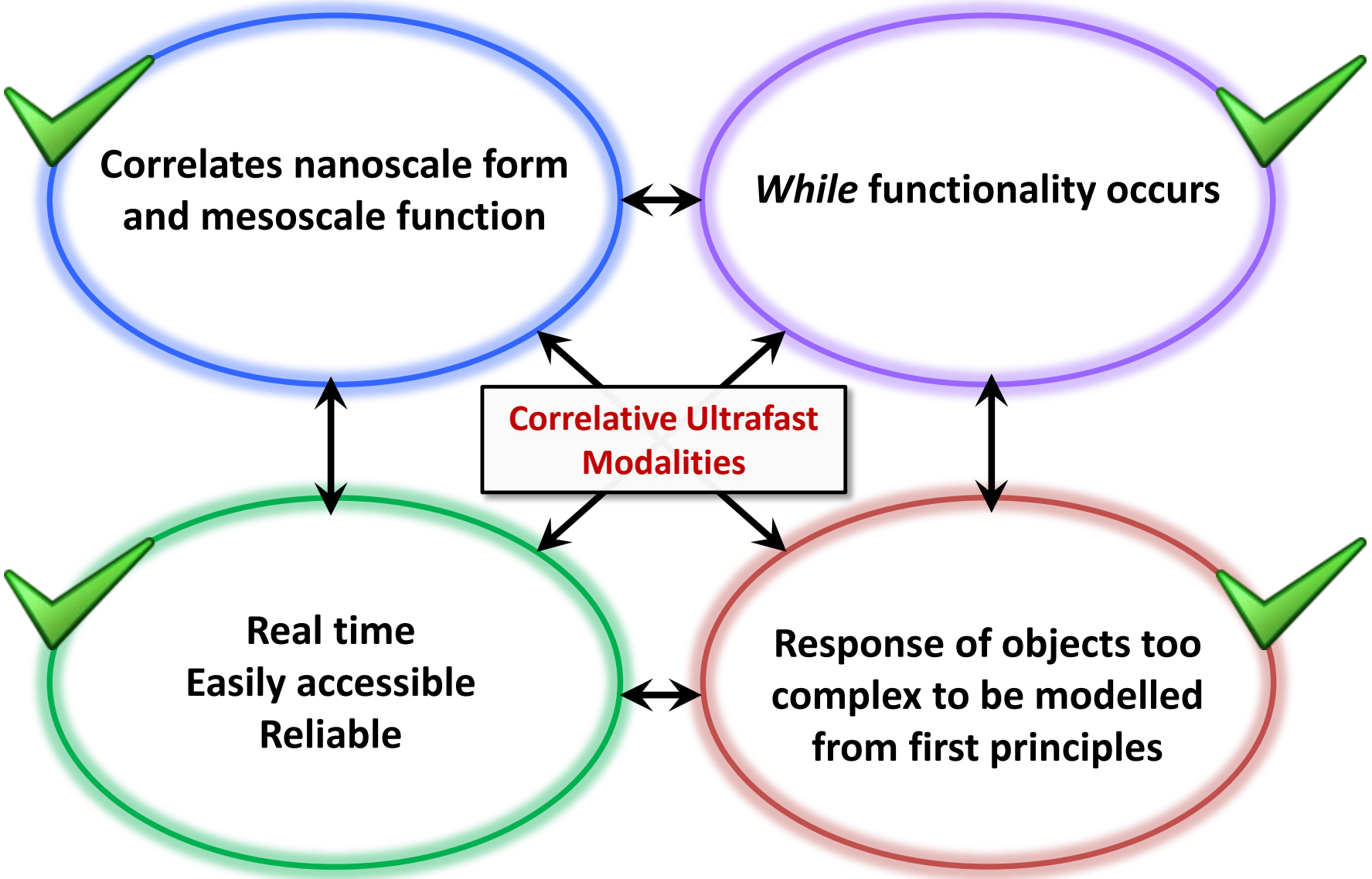
Visualizing thermal and acoustic dynamics





- **Average height changes by ≈3Å in agreement with experiment**
- Dispersion of generalized **Lamb waves**
- **Surface acoustic waves** propagating across the nanoantenna **coupled into dispersive wave guide modes**

Next frontier: probing heterogeneity



Frontiers of Ultrafast X-ray Spectroscopy and Imaging

OSA Virtual Seminar

Questions?

giuliafulvia.mancini@unipv.it

Open PhD & PostDoc positions!