# Making Molecular Movies with MeV Electrons

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FRIB

ACCELERATOR PHYSICS
AND ENGINEERING SEMINARS
Dec. 17th, 2021

SLAC NATIONAL ACCELERATOR LABORATORY

# Outline

- Introduction
- SLAC MeV UED
- Science highlights
- R&Ds

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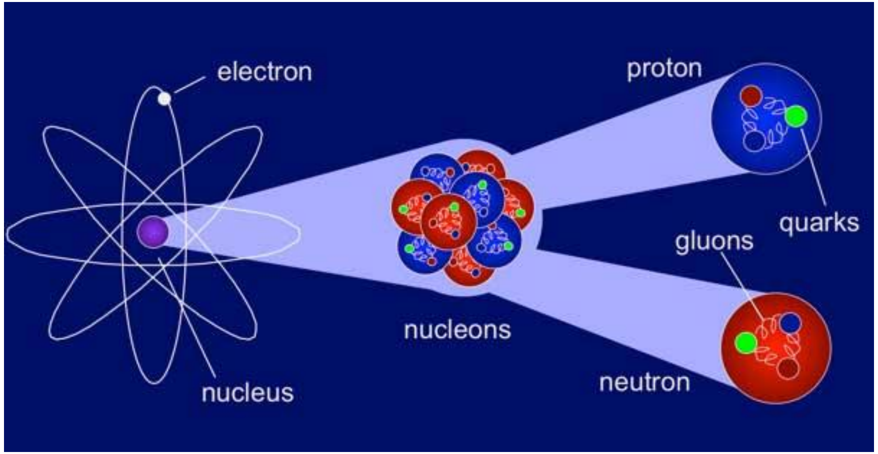
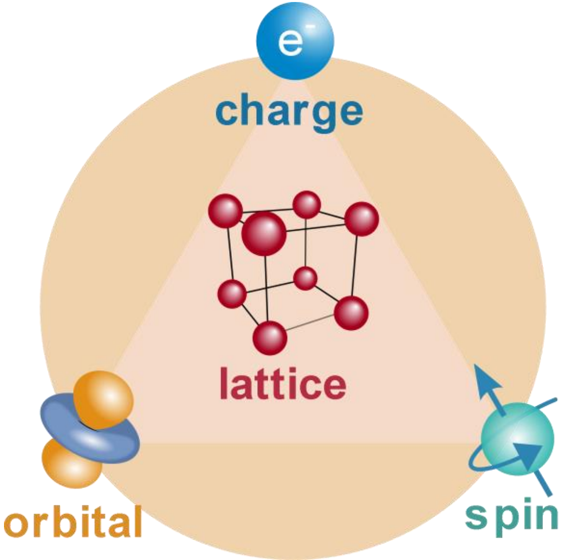
# A brief comparison of objectives




One of the main missions of FRIB is to answer

- "*How does **subatomic matter** organize itself and what phenomena emerge?*"

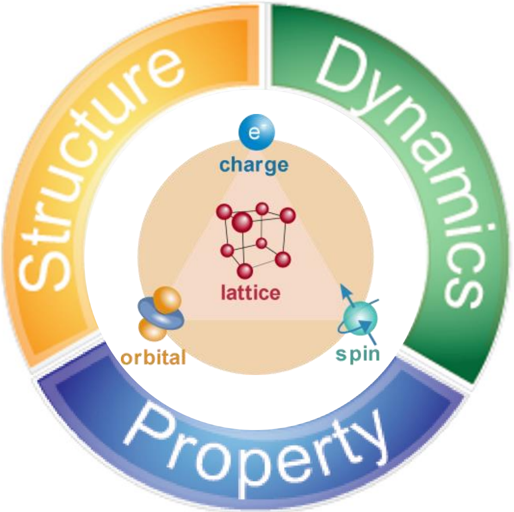
Quoted from *FRIB: Opening New Frontiers in Nuclear Science – Moving Forward with the Long Range Plan* (https://frib.msu.edu/_files/pdfs/frib_opening_new_frontiers_in_nuclear_science.pdf)

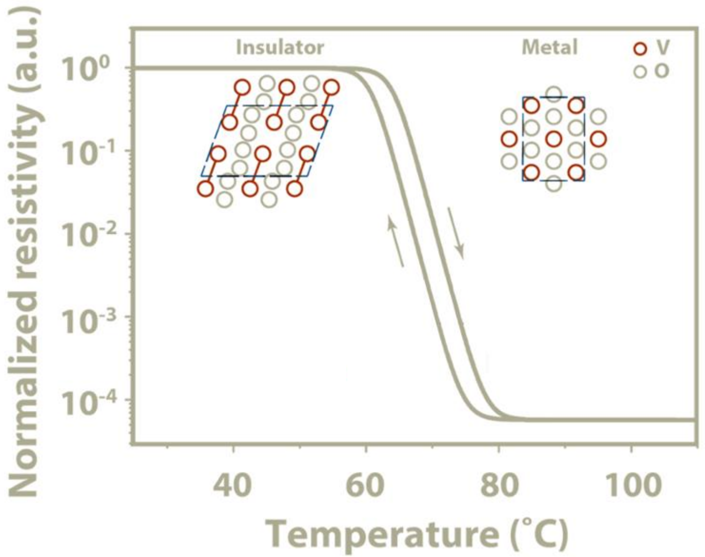



**Atomic scale** objectives in matter

- Lattice, electron, orbital, spin degrees of freedom in crystals

# Structure-property-dynamics correlation



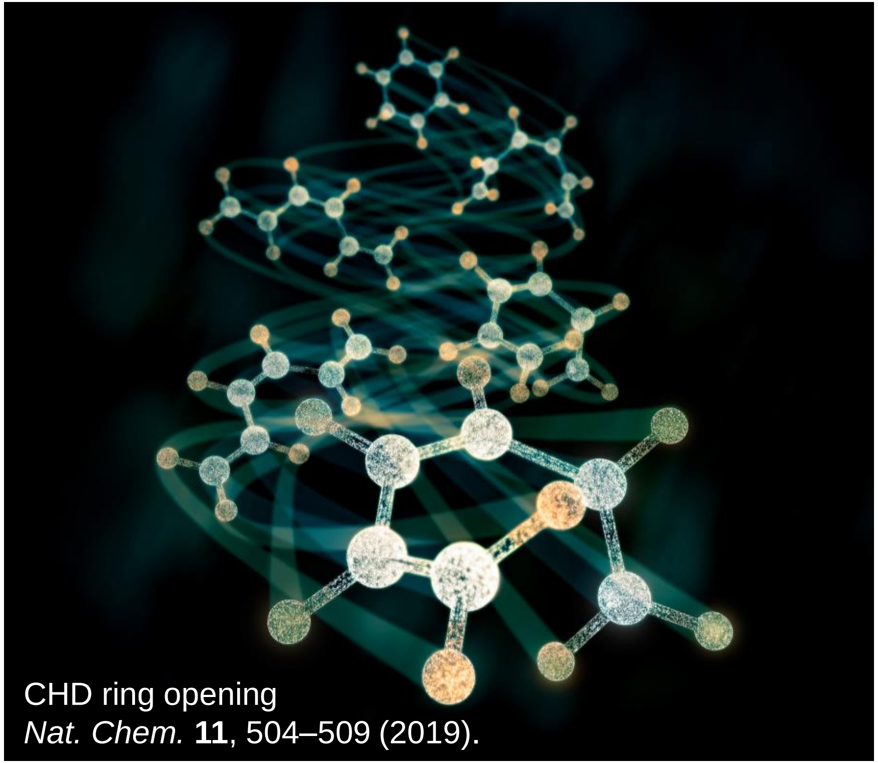




- Structure – spatial scale Angstrom ($10^{-10}$m)
- Property – insulator, metal, superconductor, …
- Dynamics -- temporal scale femtosecond ($10^{-15}$ s)
- Structure-property-dynamics correlation → full understanding and controlling of energy and matter

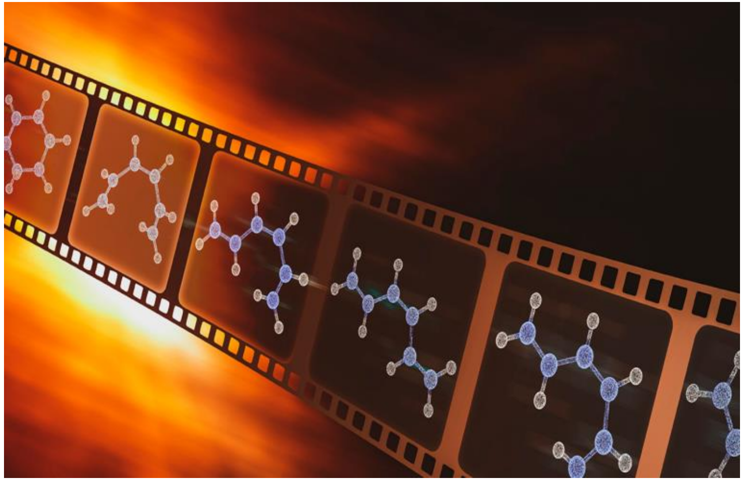
- **Metal-insulator phase transition** in $VO_2$
  - Monoclinic lattice – insulator
  - Rutile lattice – metal

# Molecular movie

SLAC

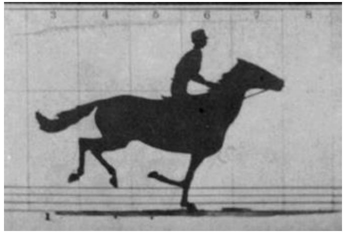


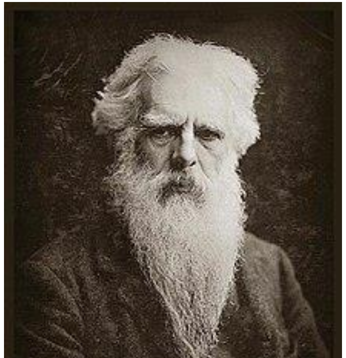
CHD ring opening
*Nat. Chem.* **11**, 504–509 (2019).



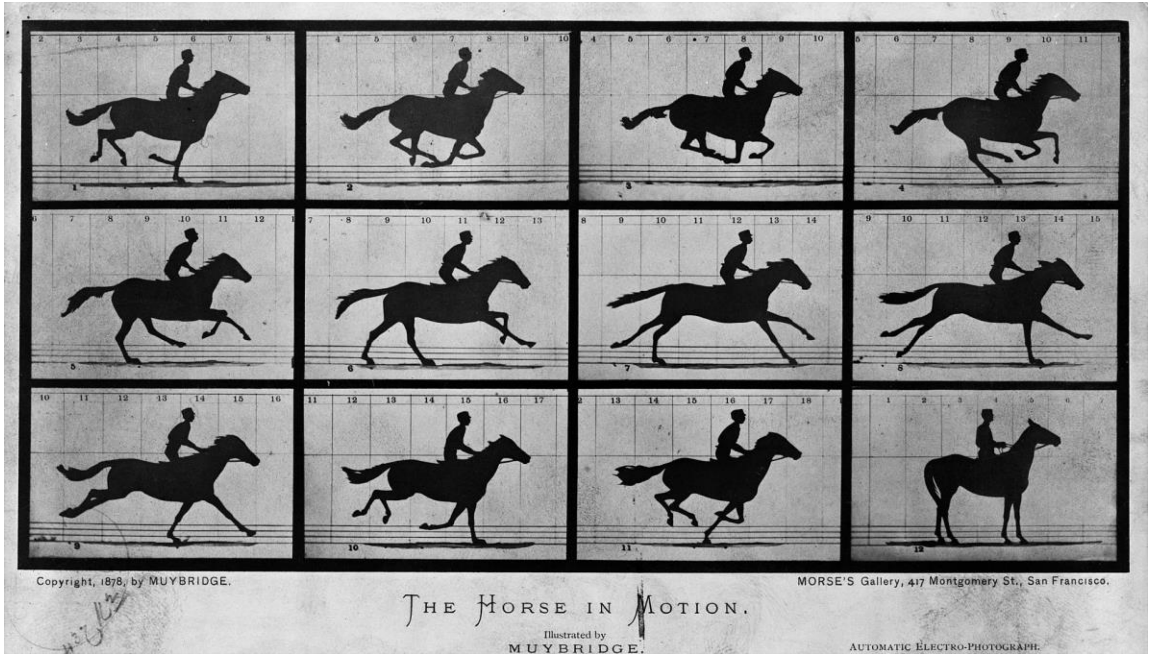
- Reveal structure-property-dynamics correlation
- Require atomic length (Å) and time scale (fs) resolutions

# First stroboscopic photography





Eadweard Muybridge

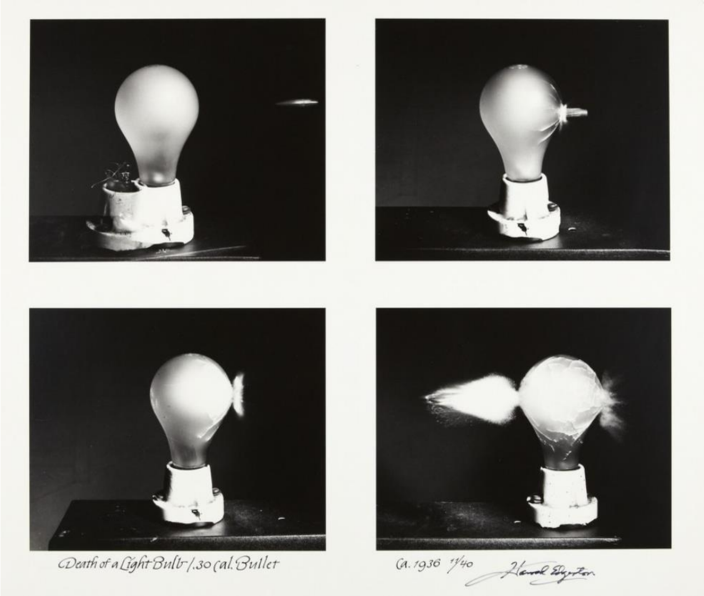



- The motion of a galloping horse is too fast to be captured by human eyes
- "*All four legs of a galloping horse are off the ground momentarily*"?
- An array of 12 cameras photographing a galloping horse in a sequence of shots
- Time resolution **~100 ms**

# High-speed stroboscopic photography


Harold Eugene Edgerton

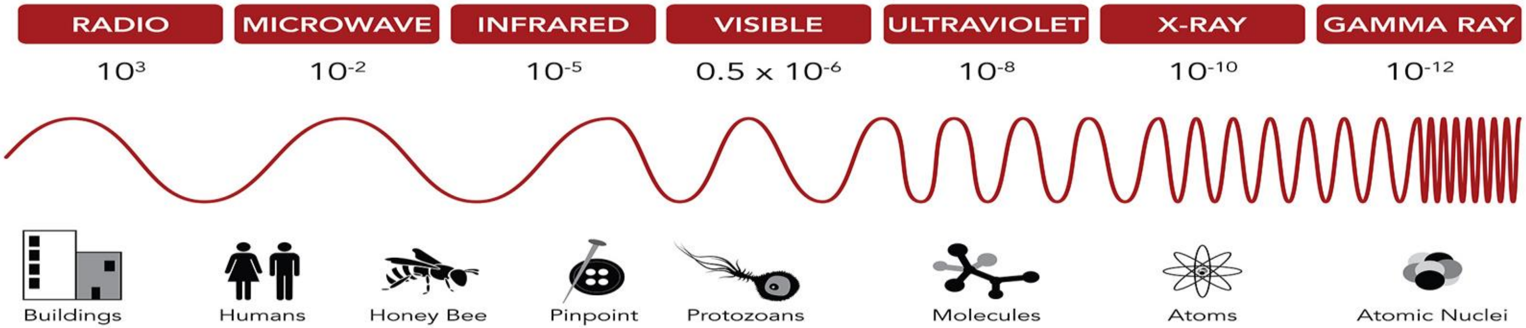

*Milk Drop Coronet,* 1935



*Death of a light bulb,* 1936

- Use a flashing light (strobe) to stop motion, reach a time resolution on the order of **μs,**
- Provide new insights into fast dynamics (first pump-probe experiment). *(https://youtu.be/yIUZ-qKWnXc)*

# Probing ultrafast and ultrasmall with lights

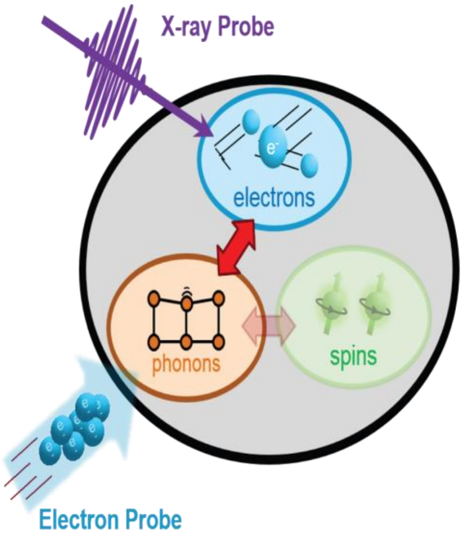


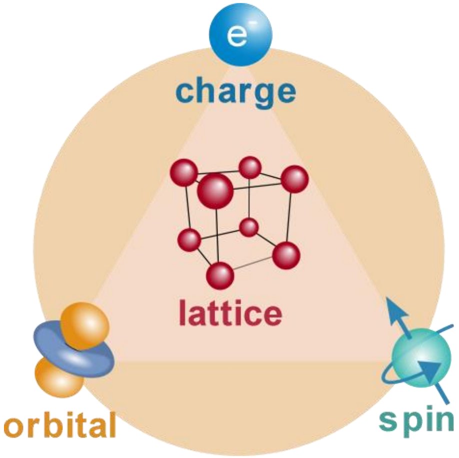


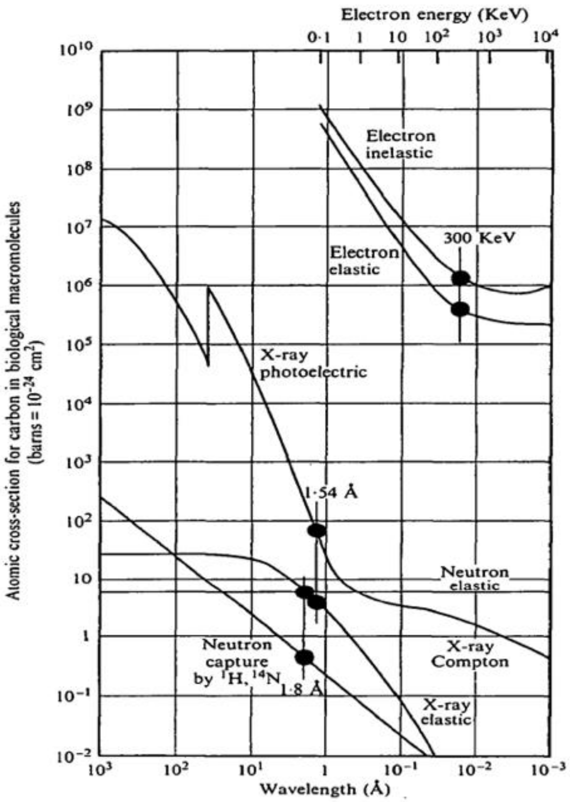
Stanford Synchrotron Radiation Lightsource (SSRL). **234 m** circumference.

Linac Coherent Light Source (LCLS). 3200 m long.

# Probing ultrafast and ultrasmall with electrons



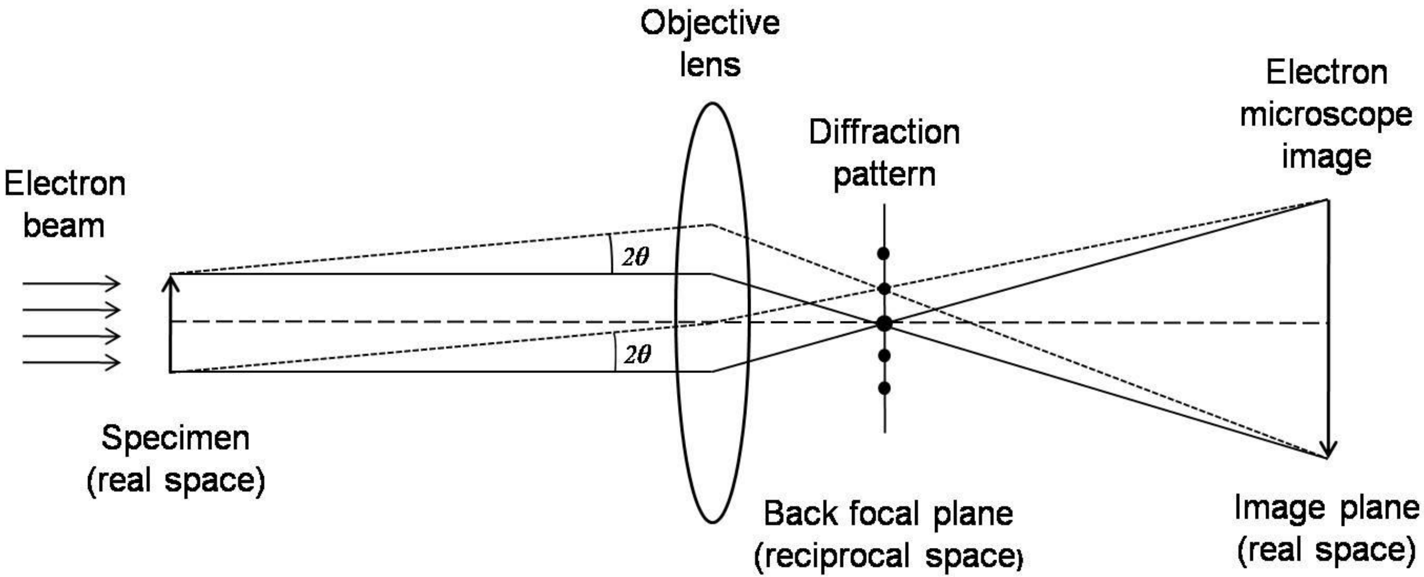




Unique features of electron compared to x-ray

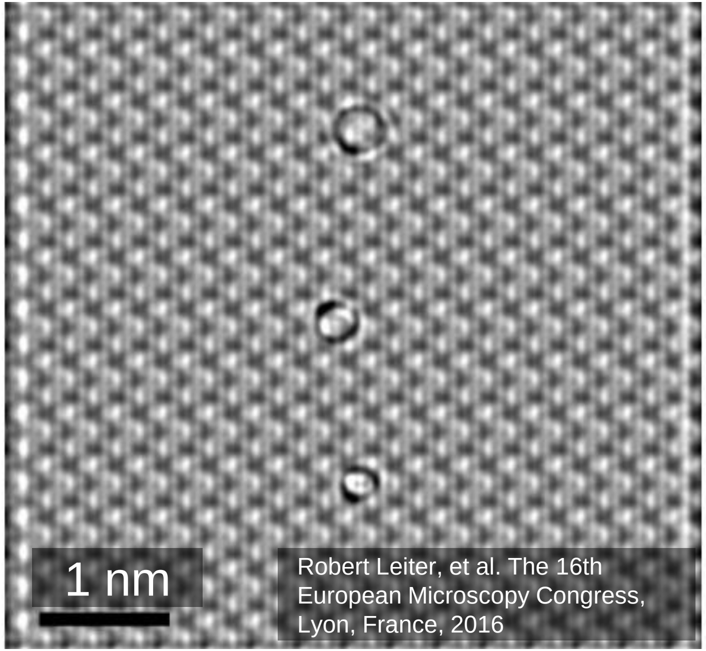
- $10^4 - 10^6$ times larger scattering cross sections
- $10^3$ times less radiation damage
- charged particle, flexibly manipulated by electromagnetic fields

R. Henderson, *Q. Rev. Biophys*. **28**, 171 (1995).

# Real space vs diffractive (reciprocal space) imaging

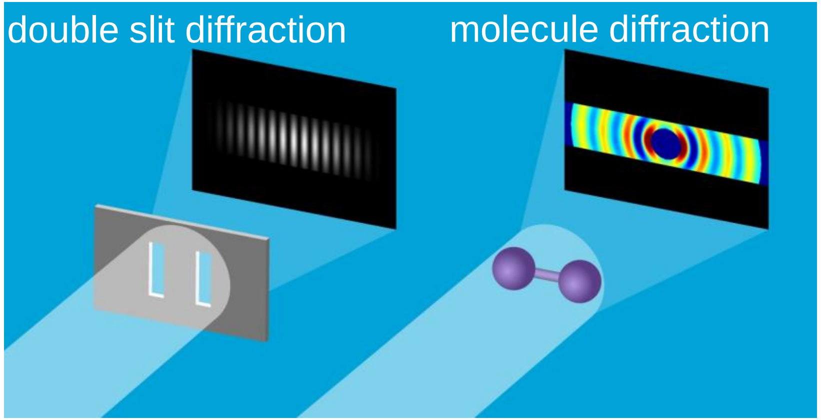


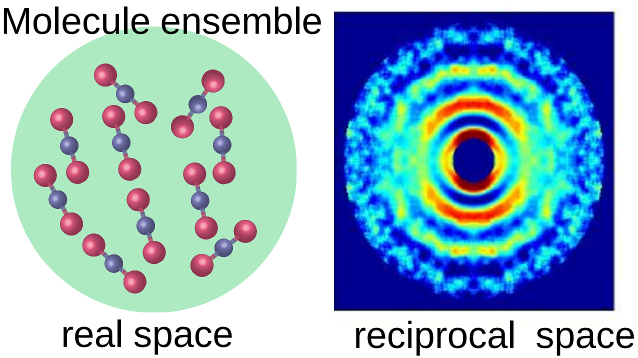
# Real space imaging



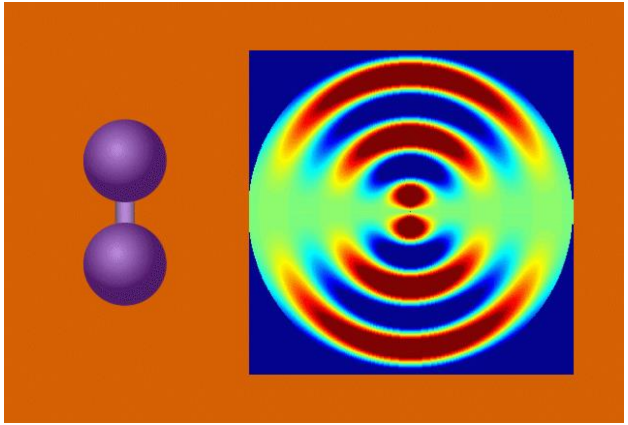

- Good at resolving local structure, such as defects, dislocations, etc.
- Can reach Å spatial resolution with sophisticated aberration correction optics
- Not yet reaching fs temporal resolution at the same time

# Diffractive (reciprocal space) imaging




- Conjugated to real space imaging
- Ensemble average imaging
- Can reach Å-fs spatial-temporal resolution



# First ultrafast electron diffraction experiment

**Prof. Gérard Albert Mourou**
*recipient of 2018 Nobel Prize for physic "for his invention of chirped pulse amplification"*

Mourou et al., *Appl. Phys. Lett*. **41**, 44 (1982)
Williamson et al., *Phys. Rev. Lett*. **52**, 2364 (1984)

Ultrafast (20 ps) melting of Al thin film

- 25 keV electron beams
- Laser pump electron probe experiment
- 100 samples per pump-probe delay point

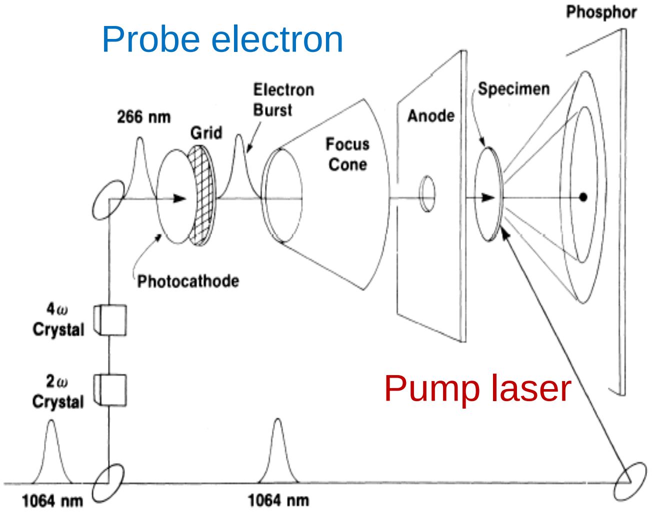
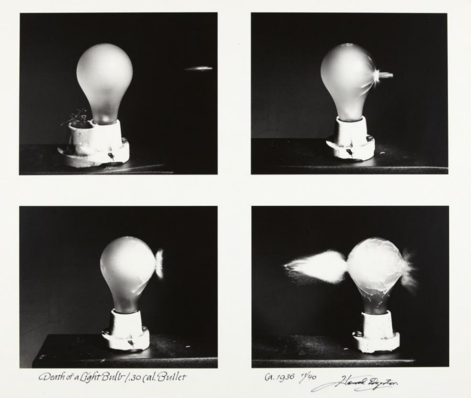
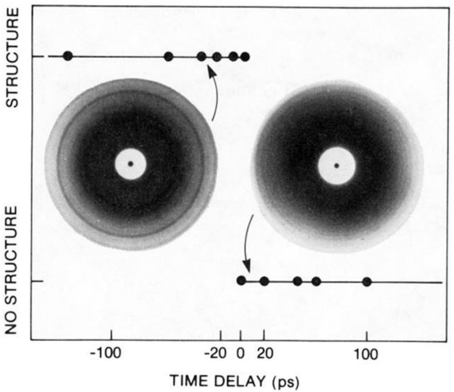



FIG. 1. Schematic of picosecond electron-diffraction apparatus. A streak-camera tube (deflection plates removed) is used to produce the electron pulse. The 25-keV electron pulse passes through the Al specimen and produces a diffraction pattern of the structure with a 20-ps exposure.





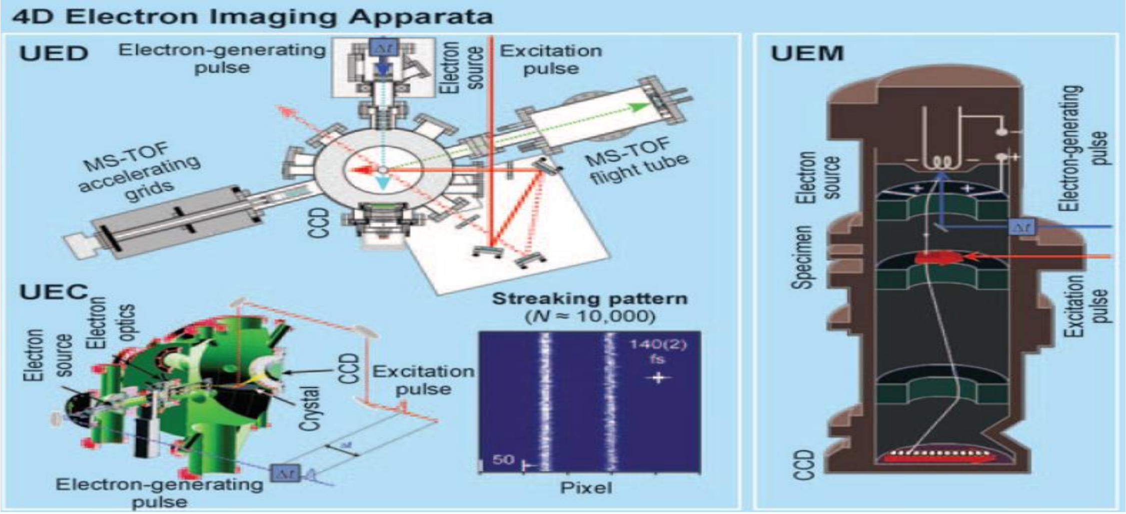
# Development of UED/UEM

**Prof. Ahmed Hassan Zewail,** *recipient of 1999 Nobel Prize in Chemistry, "for showing that it is possible with rapid laser technique to study in slow motion how atoms in a molecule move during a chemical reaction"*

**Gas phase UED**, femto-chemistry, 0.01Å, 1 ps

**Ultrafast electron crystallography**, picometer, 300 fs

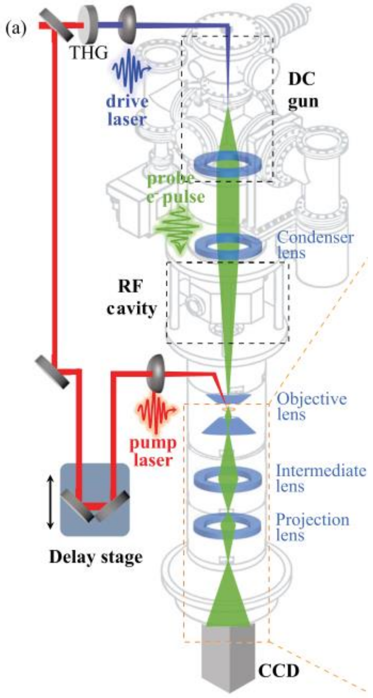
**Ultrafast electron microscopy**, single-electron, ≤ 100 fs




A. H. Zewail, *Annu. Rev. Phys. Chem.* 2006, 57, 65

# Development of UED/UEM

- Higher time resolution (~100 fs)
  - Short electron propagation distance (1-5 cm)
  - Radio-frequency compression cavity
- Higher beam coherence
  - Nanotip cathode emission
- Profs. R. J. D Miller, Bradley Siwick, Ralph Ernstorfer, Claus Ropers, Jianming Cao, David Flanagan, Chong-Yu Ruan,…




**Prof. Chong-Yu Ruan**
Department of Physics and Astronomy, Michigan State University

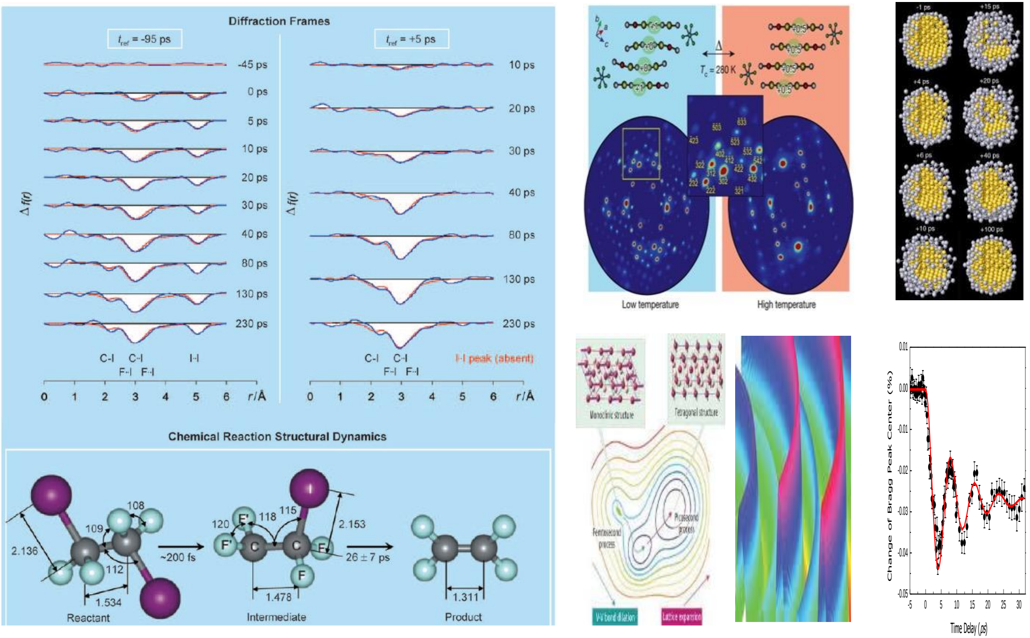
S. Sun *et al.*, *Structural Dynamics*. **7**, 064301 (2020).

# Development of UED/UEM

Applications:

- Gas phase electron diffraction
- Strain waves/phonons
- Phase transitions (irreversible)
- Correlated electron materials
- Surfaces, interfaces
- Nanoparticles (~2 nm)
- Complex molecular crystals

Electron probe energies are on **keV level** due to the DC voltage breakdown limit




M. Chergui, *et al. ChemPhysChem* **10**, 28–43 (2009)

# MeV electrons for UED and UEM

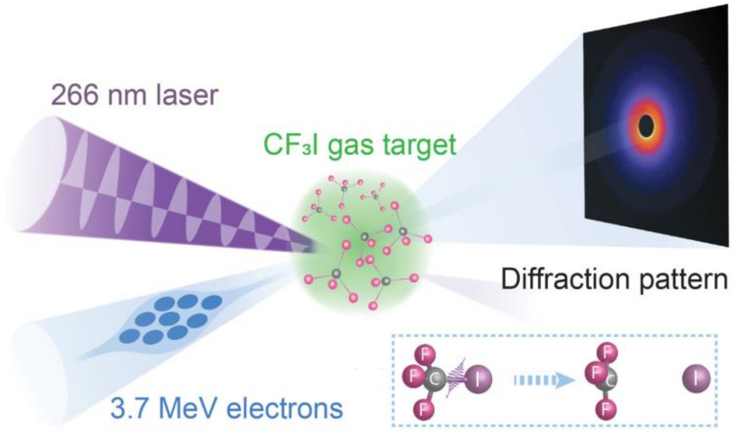
Space-charge forces suppression with relativistic electrons

- shorter bunch ⇒ higher time resolution
- more electrons in a bunch


$\propto \frac{1}{\beta^2\gamma^3}$

Negligible pump-probe velocity mismatch

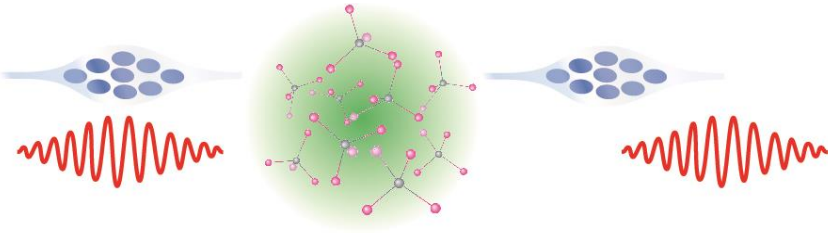
- $\Delta t_{vm}$<10 fs for 3 MeV e beam passing 150 $\mu$m gas target




60 keV e-
$\beta = 0.45$

gas target
150 um

$\Delta t_{vm} > 1\text{ps}$



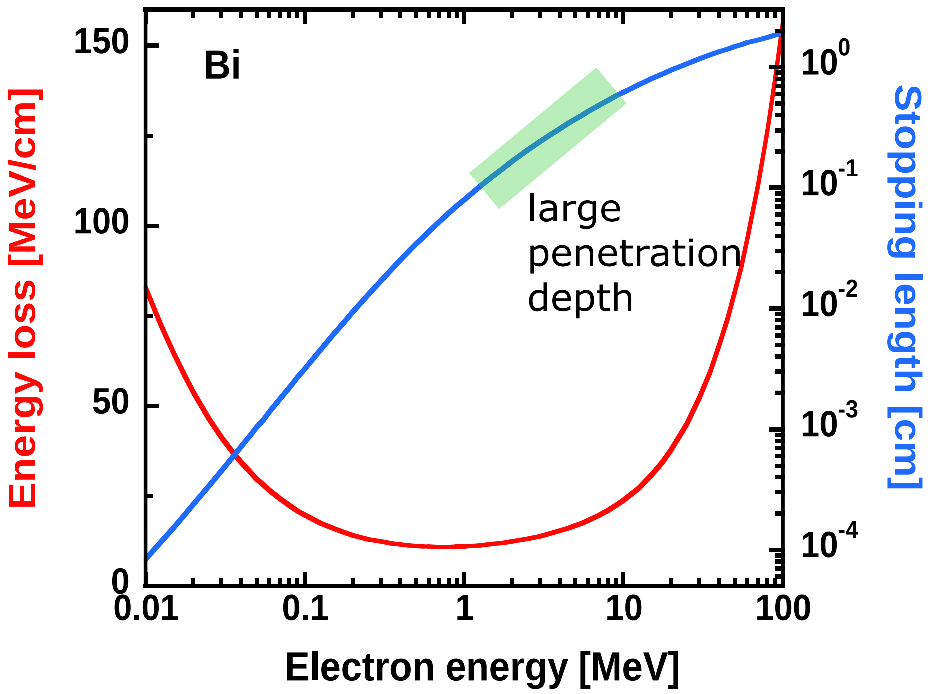
# MeV electrons for UED and UEM

Larger penetration depth

- “thick” sample
- kinematic diffraction

Less sample damage

- Less energy deposition
- Lower dose rate, less damage to dose rate sensitive matter




physics.nist.gov/PhysRefData/Star/Text/ESTAR.html

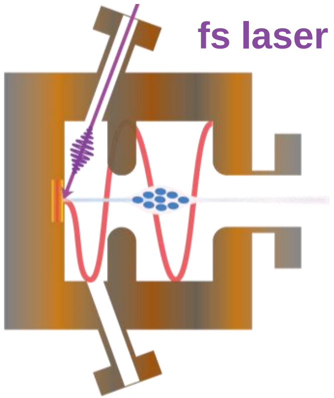
# MeV electrons for UED and UEM

Development of femtosecond laser system
- triggering generation of ultrashort photoelectrons

Advancement in high gradient photocathode radio-frequency (RF) gun
- Rapid acceleration of photoelectrons to relativistic energy

Numerous research efforts over decades

Currently active MeV UED/UEM programs
- SLAC, BNL @USA, DESY @Germany, SJTU @China, KAIST @Korea, Osaka Univ. @ Japan




PHYSICAL REVIEW E VOLUME 54, NUMBER 4 OCTOBER 1996

**Experimental observation of high-brightness microbunching in a photocathode rf electron gun**

X. J. Wang, X. Qiu, and I. Ben-Zvi
*National Synchrotron Light Source, Brookhaven National Laboratory, Upton, New York 11973*
(Received 13 February 1996)

We report the measurement of very short, high-brightness bunches of electrons produced in a photocathode rf gun with no magnetic compression. The electron beam bunch length and the charge distribution along the bunch were measured by passing the energy chirped the electron beam through a momentum selection slit while varying the phase of the rf linac. The bunch compression as a function of rf gun phase and electric field at the cathode were investigated. The shortest measured bunch is 370±100 fs (at 95% of the charge) with $2.5\times10^8$ electrons (170 A peak current); the normalized rms emittance of this beam was measured to be $0.5\pi$ mm mrad and the energy spread is 0.15%. [S1063-651X(96)51110-4]

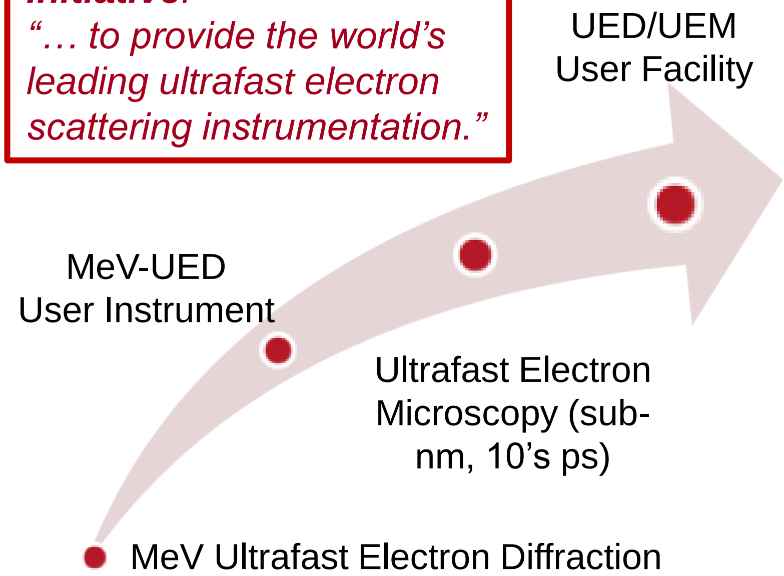
**Dr. Xijie Wang**, *recipients of the 2021 PAST Award, bestowed by the Institute of Electrical and Electronics Engineers, IEEE.*
"for contributions to the development of high-brightness, ultrafast electron beams and their applications to free-electron lasers and ultrafast electron diffraction."

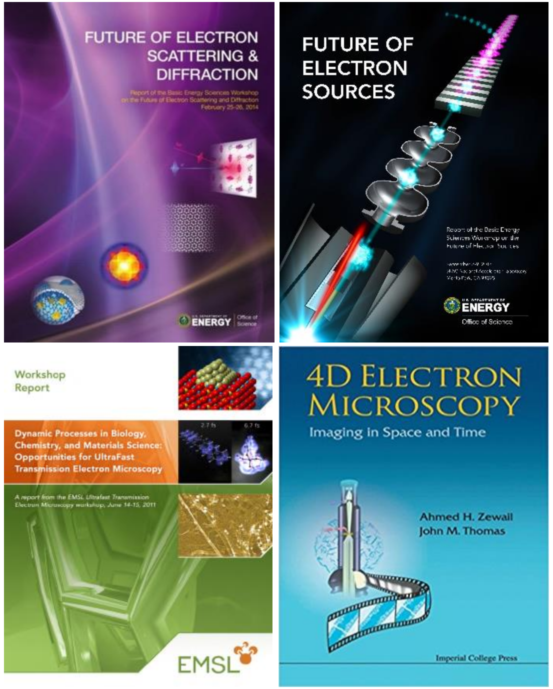
# Outline

- Introduction
- SLAC MeV UED
- Science highlights
- R&Ds

# SLAC's vision for ultrafast electron scattering

***SLAC UED/UEM Initiative**:*
*"… to provide the world's leading ultrafast electron scattering instrumentation."*




Development of ultrafast electron scattering instrument to enable advanced scientific opportunities

# SLAC's vision for ultrafast electron scattering

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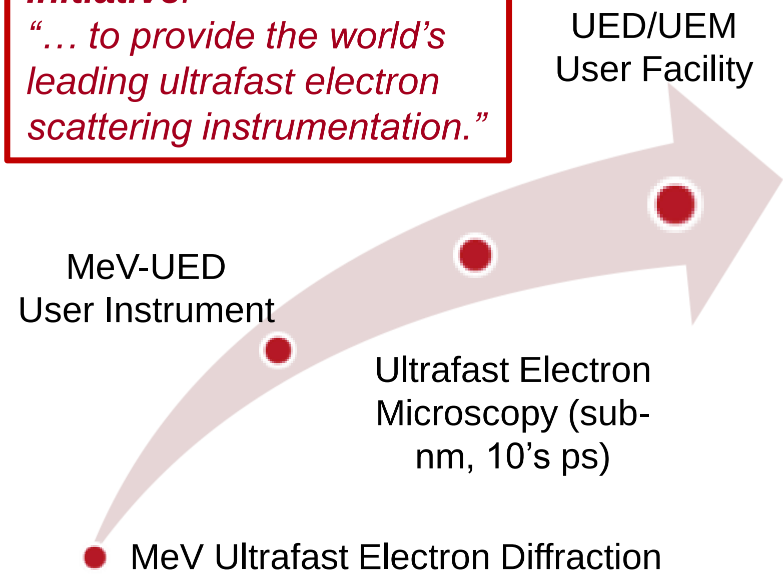
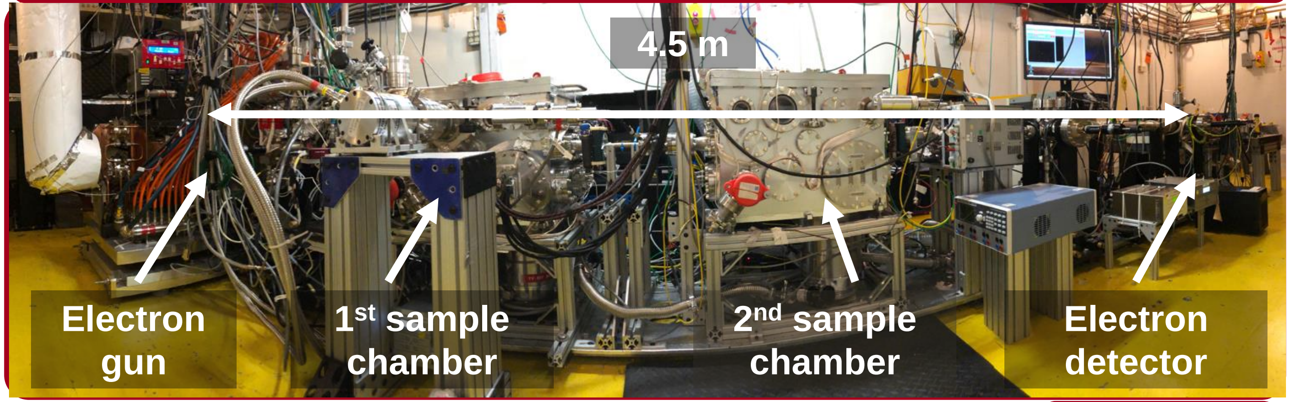



| | |
|---|---|
| **Apr 2014** | **UED program launched** |
| **Mar 2015** | **Gas-phase UED** |
| **Mar 2016** | **Single-shot UED** |
| **Jun 2017** | **THz Mid-IR UED** |
| **Jan 2019** | **UED user facility** |
| **Apr 2019** | **First liquid-phase UED** |

# Instrument overview

## SLAC MeV UED beamline layout




| | |
|---|---|
| **Rep rate** | single shot - 360 Hz |
| **Beam energy** | 2 – 4 MeV |
| **Beam charge** | $10^4 – 10^6$ |
| **Beam emittance** | 2–20 nm·rad |

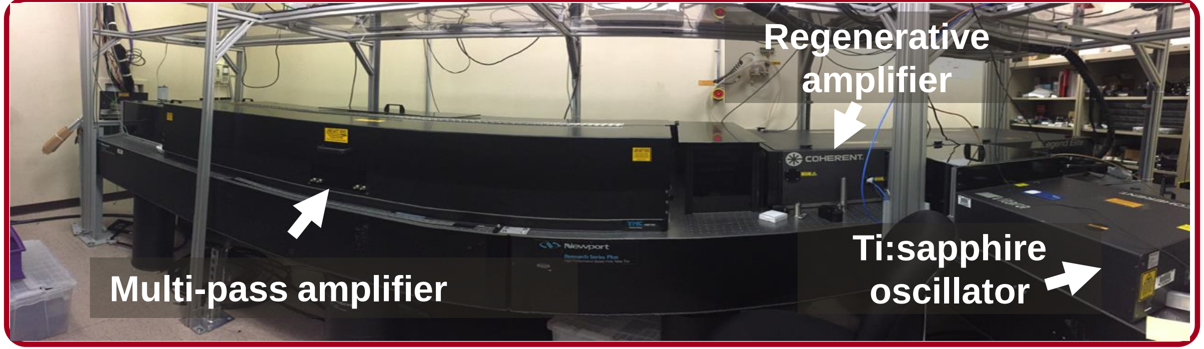
| | |
|---|---|
| **Q range (with $2\pi$)** | 12 Å$^{-1}$ |
| **Q res. (FWHM)** | 0.17 Å$^{-1}$ |
| **Time res. (FWHM)** | < 150 fs |
| **Stability** | NON-STOP ops>5 days |

S. Weathersby, *et al.*, *Rev. Sci. Instrum.* ***86****, 73702 (2015)*)

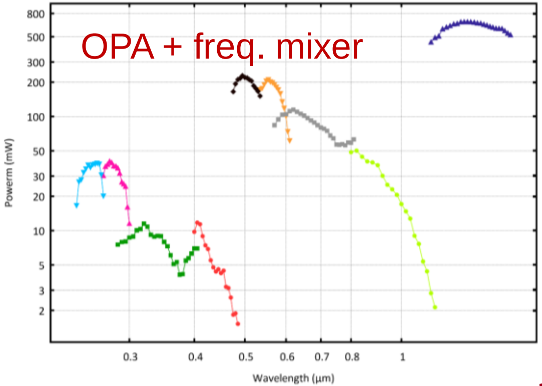
X. Shen, *et al.*, *Struct. Dyn*. **6**, 054305 (2019)

# Pump laser capability

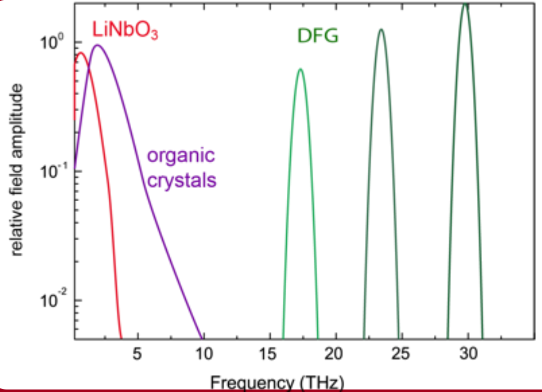
## SLAC MeV UED laser system




## Tunable UV-VIS-NIR

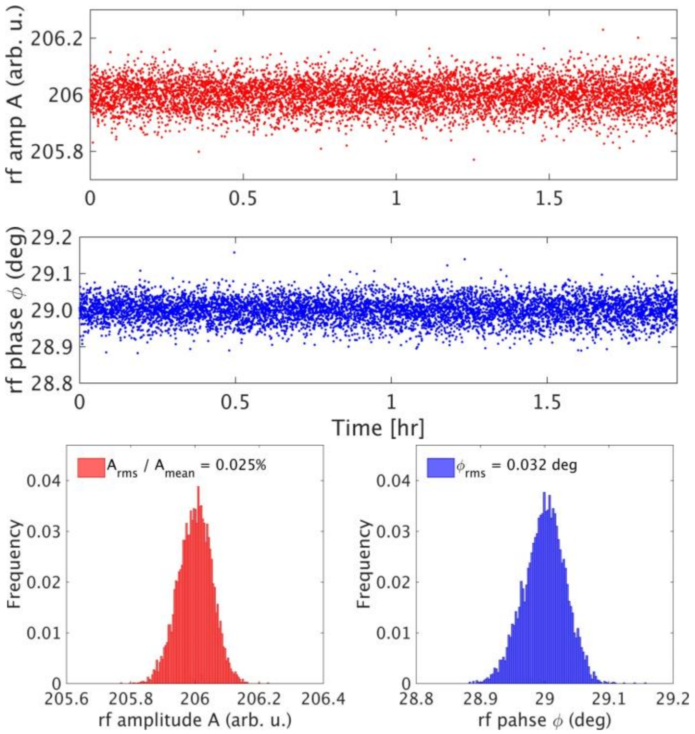



## Terahertz laser



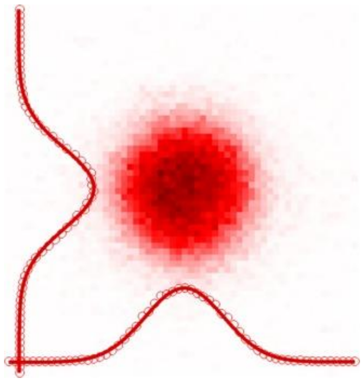
# SLAC MeV UED machine stability

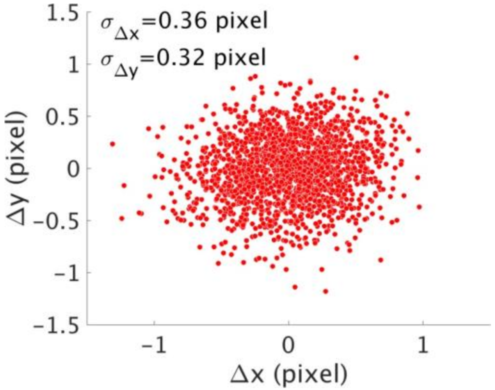
- RF stability
  - RMS rf amplitude jitter 0.025%
  - RMS rf phase jitter 0.032 deg
  - corresponds to rms timing jitter < 50 fs



# SLAC MeV UED machine stability

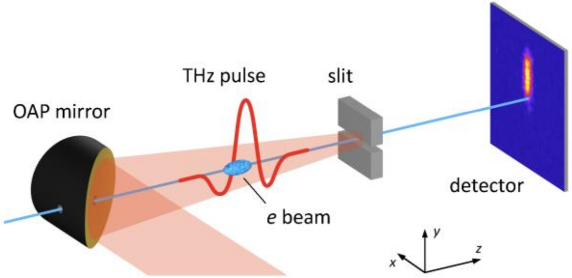
- Electron beam pointing stability
  - Single-shot e beam images at detector
  - RMS beam centroid jitters 0.36 pixel, corresponding to 10 μm.

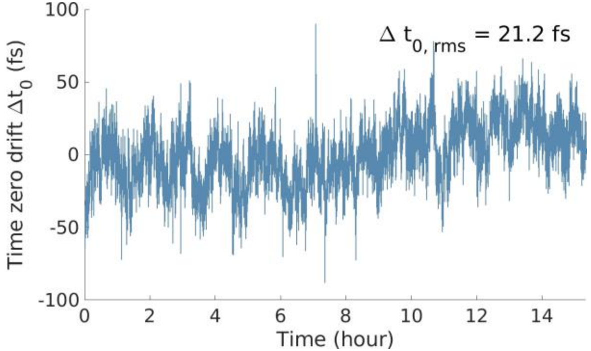




# SLAC MeV UED machine stability

- RF jitter causes electron beam arrival time jitter w.r.t. pump laser
- Pump-probe timing ($t_0$) stability
- THz streak camera* enables $t_0$ determination with < 1 fs accuracy
- Achieved rms $t_0$ jitter 21.2 fs

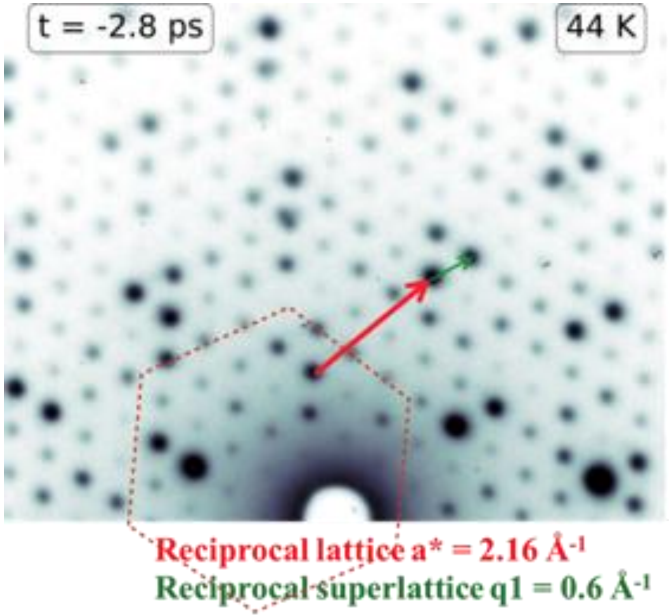



R. K. Li, et al., *Phys. Rev. Accel. Beams*, **22** 012803 (2019)

# SLAC MeV UED instrument resolutions

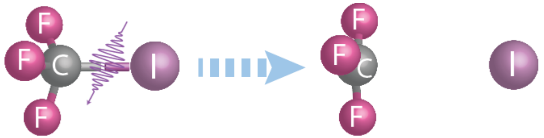
- **Reciprocal-space resolution**
  - Resolving power in reciprocal space
  - ***1T*-TaS$_2$** super lattice peaks resolved, demonstrated to be ***0.17*** $\text{Å}^{-1}$

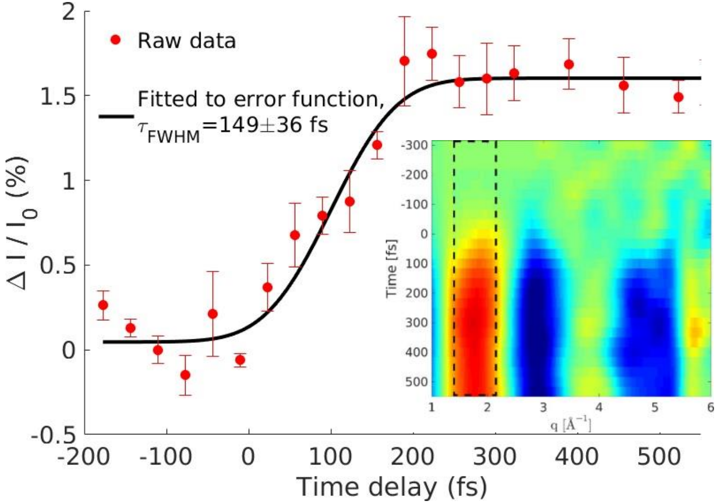



L. Le Guyader, *et al.*, *Struct. Dyn.* **4** 044020 (2017)

# SLAC MeV UED instrument resolutions

- **Temporal resolution**
  - Time-resolved photodissociation process of $CF_3I$ molecules
  - Demonstrated to be ***< 150 fs FWHM***




J. Yang, *et al.*, *Science* **361** 64-47 (2018)

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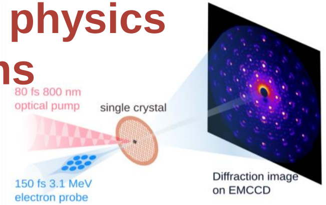
# Multifunctional platform for ultrafast science

SLAC

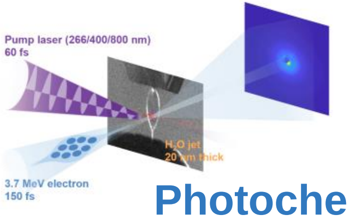
SLAC MeV UED

Solid phase · Liquid phase · Gas phase · Single shot · Electric pump

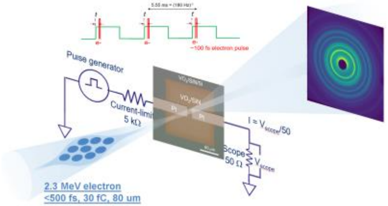
**Condensed matter physics**
**solid state thin films**



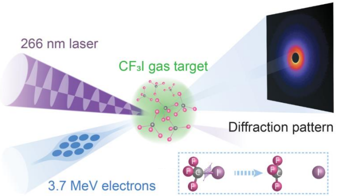

**Photochemistry**
**thin liquid jet**




**In-situ measurement**
**application device**

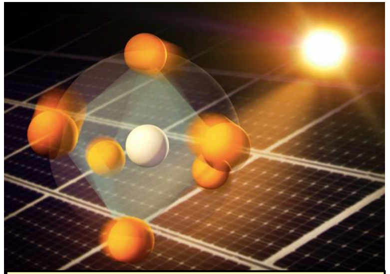



**Photochemistry**
**isolated gas molecule**

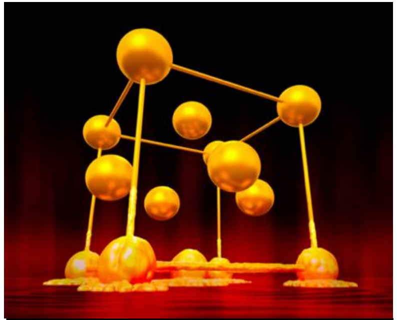



**High energy density**
**irreversible process**

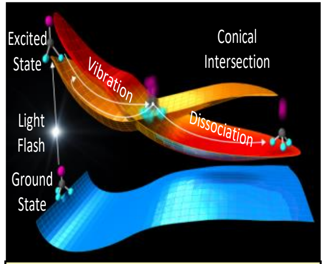
# Ultrafast science enabled by SLAC MeV UED



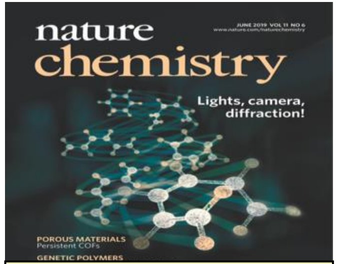
Atomic movie of light-induced structural distortion in the perovskites solar cell (***Sci. Adv.*** 3 e1602388 (2017)).



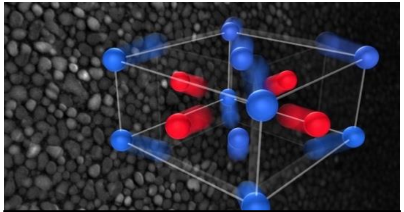
Resolving ultrafast phase transitions ***(Science 360 1451–1455 (2018))***



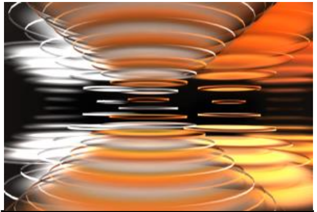

Bond-breaking & nuclear wavepacket passing through conical intersections (***Science*** *361 64–67 (2018)*)



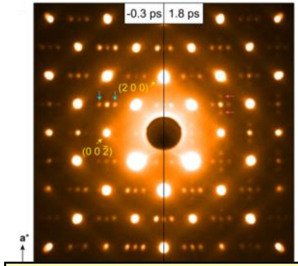

Molecular movie of ring-opening & ground state dynamics (***Nat. Chem.*** (2019)).



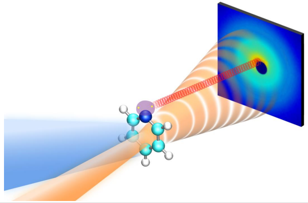
3-D FePt structure dynamics reveals lattice response to magnetic stress (***Nat. Comm. 9, 388,(2018)).***



Ultrafast topological switch by Time-varying shear strain (***Nature*** 565, 61-77 (2019))

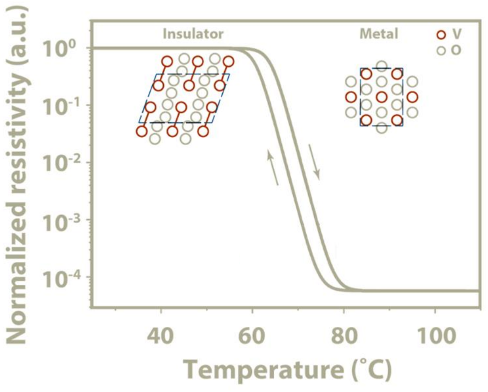



Light induced CDW (***Nat. Phys***. 16, pages159–163(2020)).

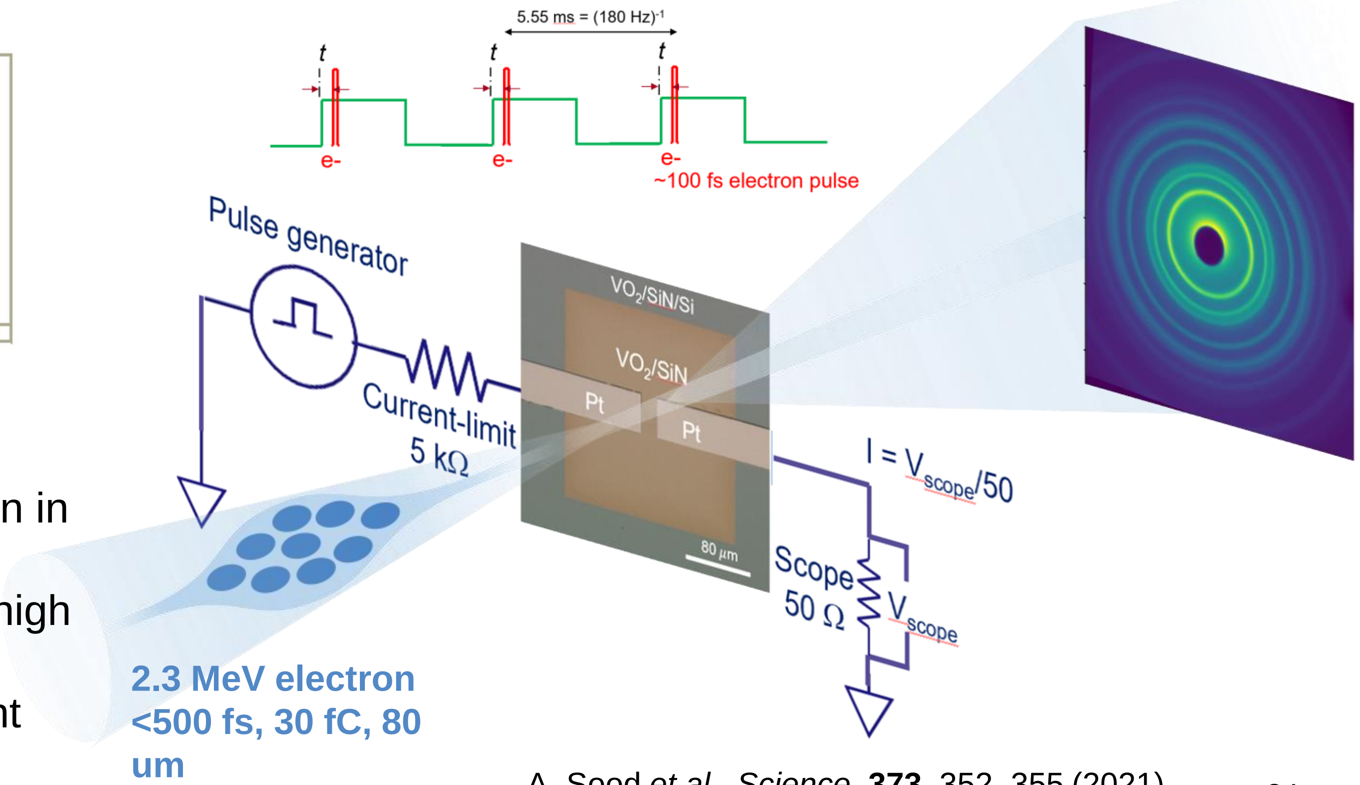


Simultaneous observation of nuclear and electronic dynamics (***Science. 368,*** 885 (2020)).

# Electric-field-pump-MeV-electron-probe schematic

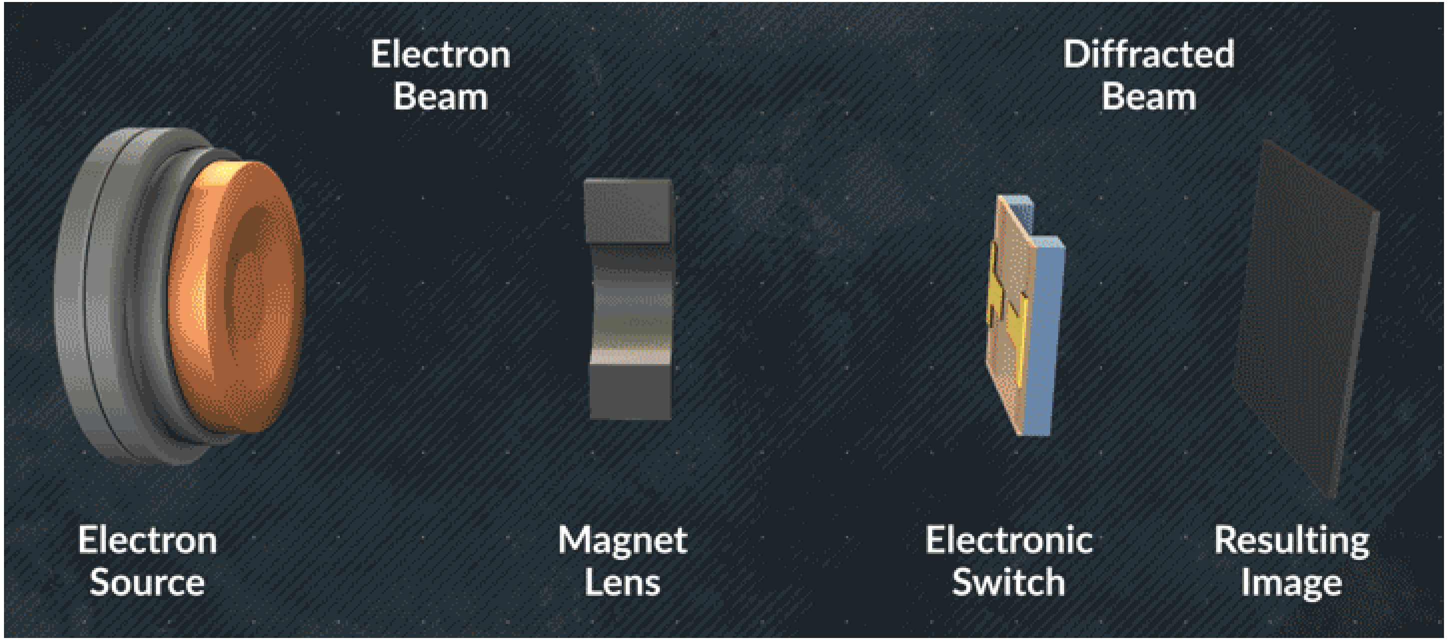



- Metal-insulator transition in $VO_2$
- Candidate material for high performance computer
- Operando measurement

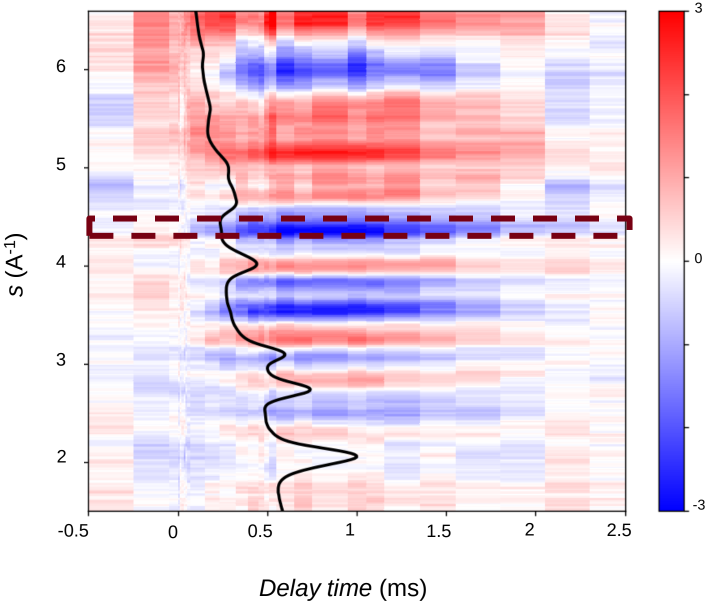


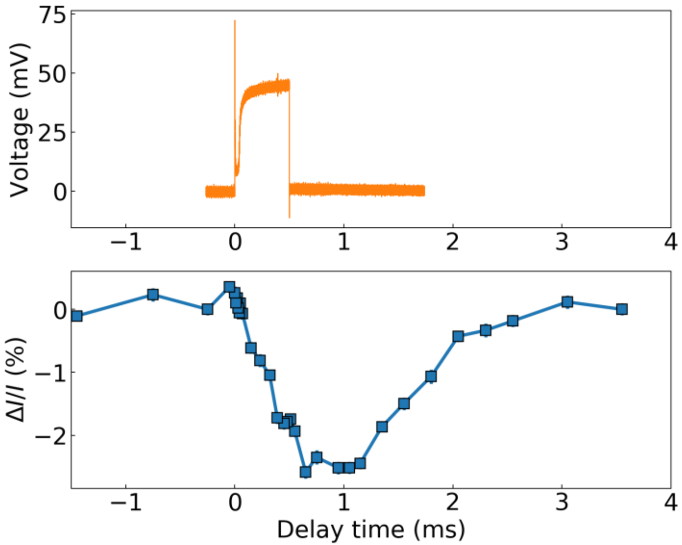

A. Sood *et al.*, *Science*. **373**, 352–355 (2021).

# Synchronized electron photography

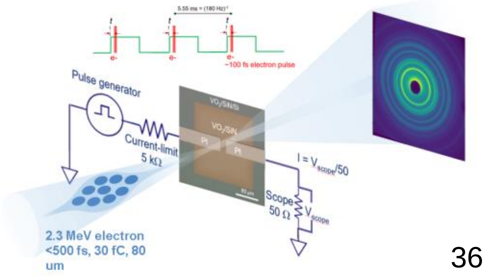


# Simultaneous structure and property measurement

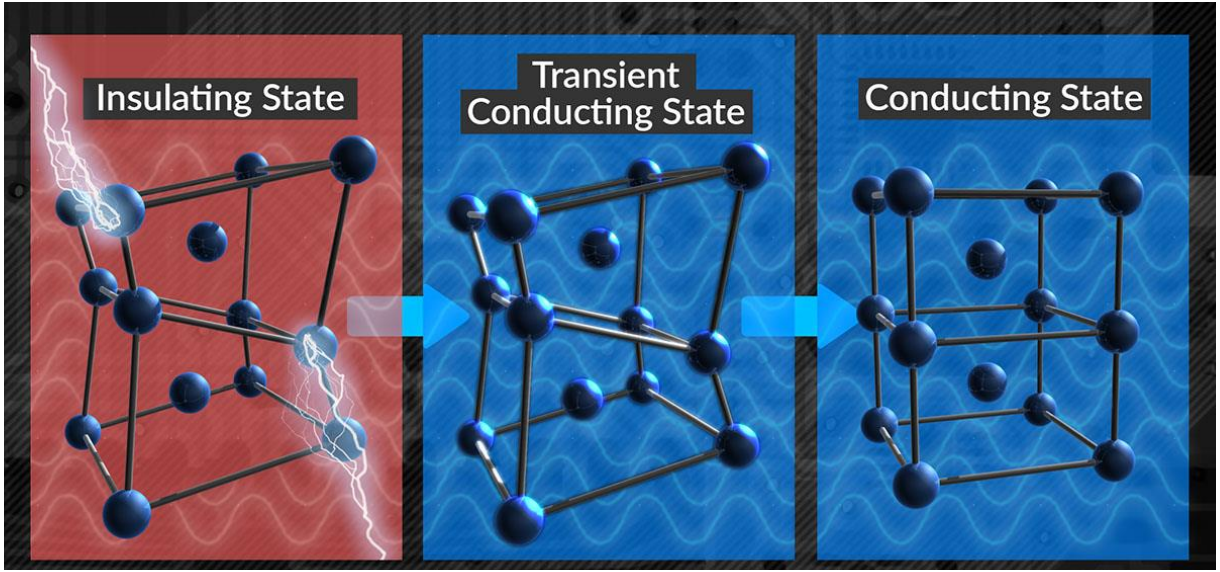


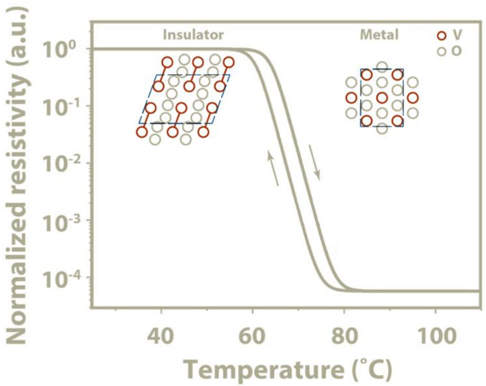




- Differential diffraction pattern reveals structure change
- Current probe measures the resistance change
- Structure-property correlation obtained



# Transient conducting state in $VO_2$

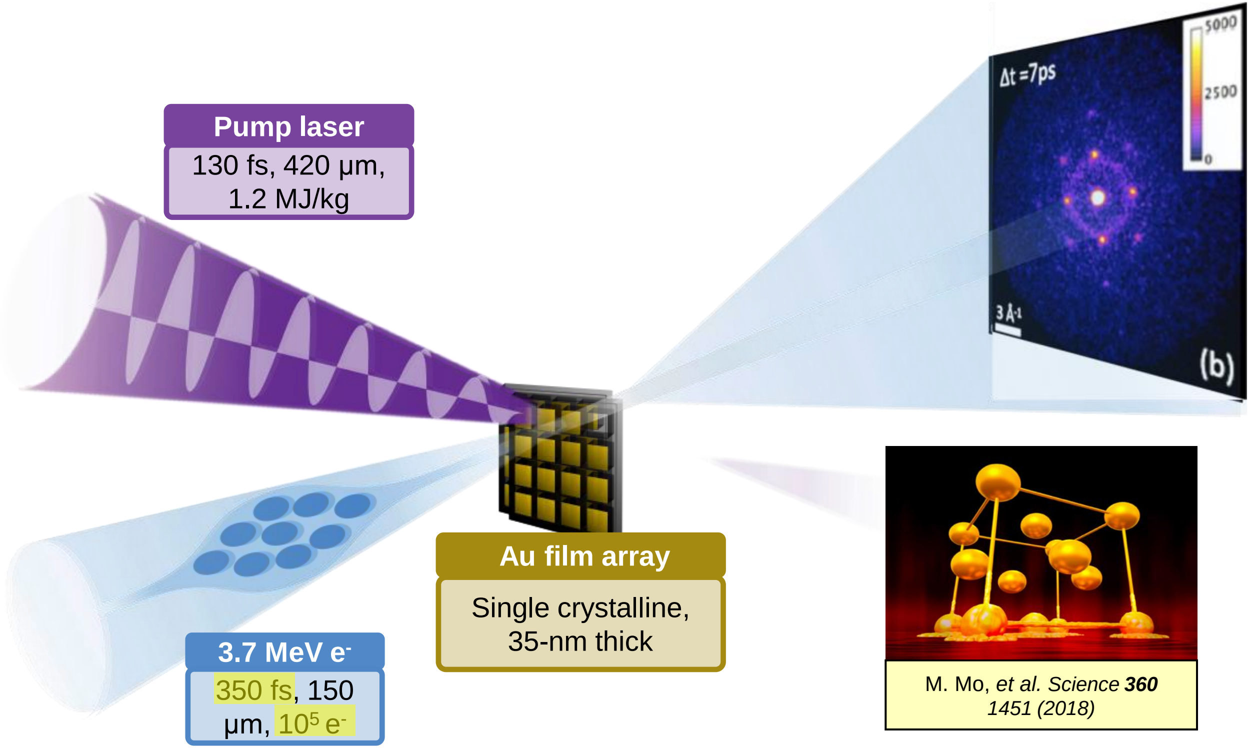



- A transient conducting state is identified
  - same lattice structure as the insulating state
  - but conducts electricity
  - Less energy to switch to, less heat, higher density computer

# Single-shot MeV UED for Au thin film melting

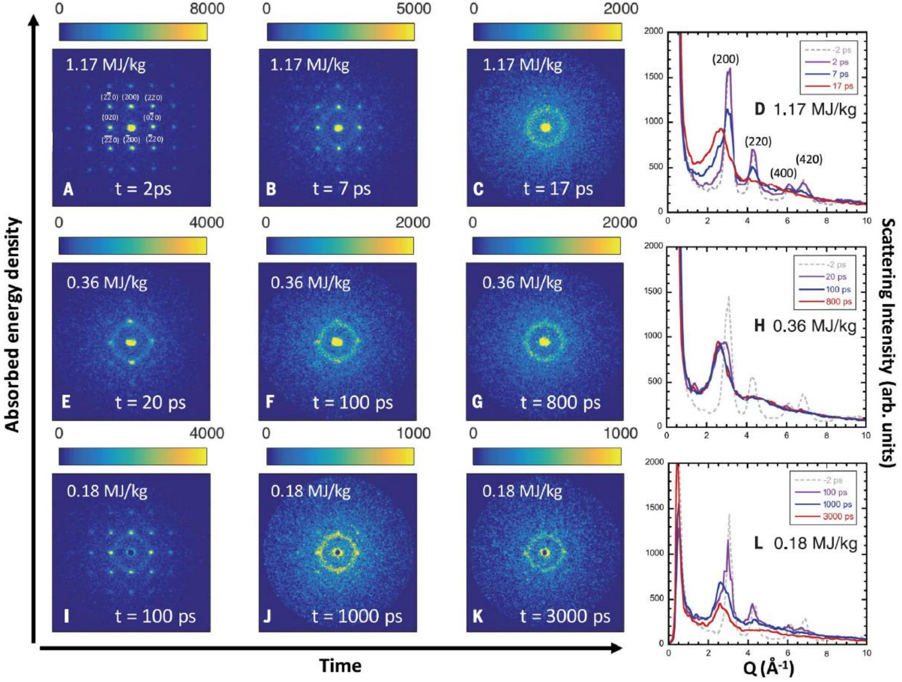
**Ultrafast irreversible melting** | High energy density science | **MeV electrons** | Single-shot diffraction

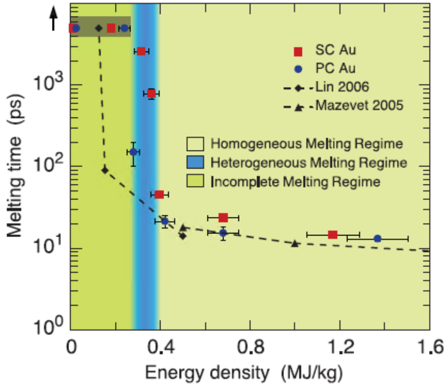



M. Mo, *et al. Science* ***360*** *1451 (2018)*

# Single-shot MeV UED for Au thin film melting

**2D diffraction** **Radial profile**




| | |
|---|---|
| **Homogeneous melting** | fast, through out sample |
| **Heterogeneous melting** | Slow, from boundary, defects |
| **Incomplete melting** | Solid-liquid coexistence |
| **Theory prediction** | Up to 60% off from experiment |

M. Mo, *et al. Science* ***360*** *1451 (2018)*

# Gas phase MeV UED

## Molecular movie

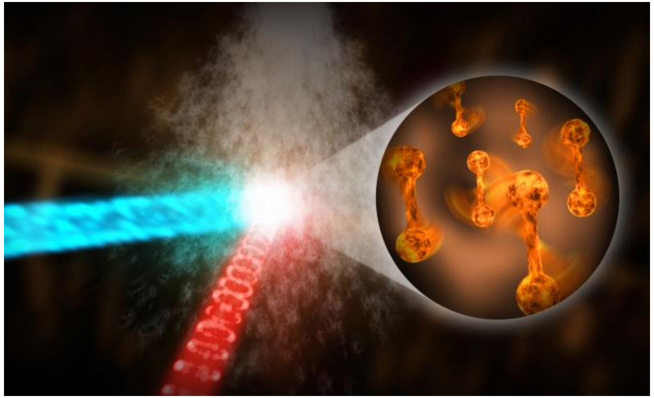
- Isolated gas molecules, photoexcitation
- Rotation, bond breaking, ring opening…
- Photoenergy conversion pathways

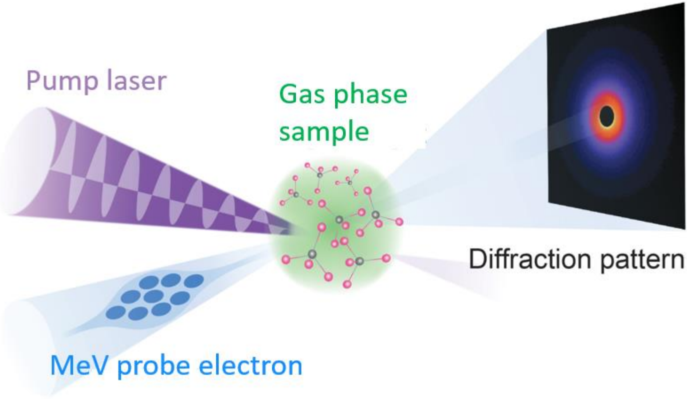
## Challenges

- Ultrafast motion (<100 fs)
- Weak gas diffraction

## MeV UED

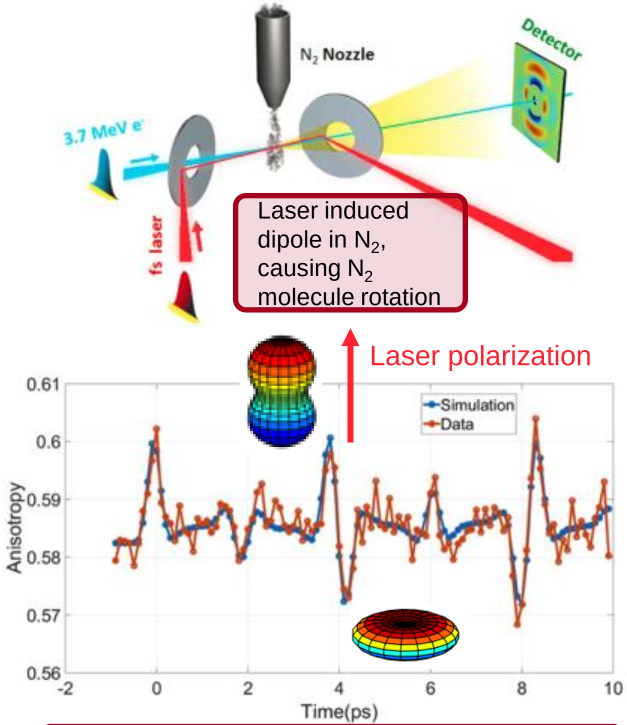
- High spatial resolution (12 $Å^{-1}$ / 0.5 Å)
- High time resolution (<150 fs)
- More $e^-$ per bunch to enhance signal





# Gas phase MeV UED

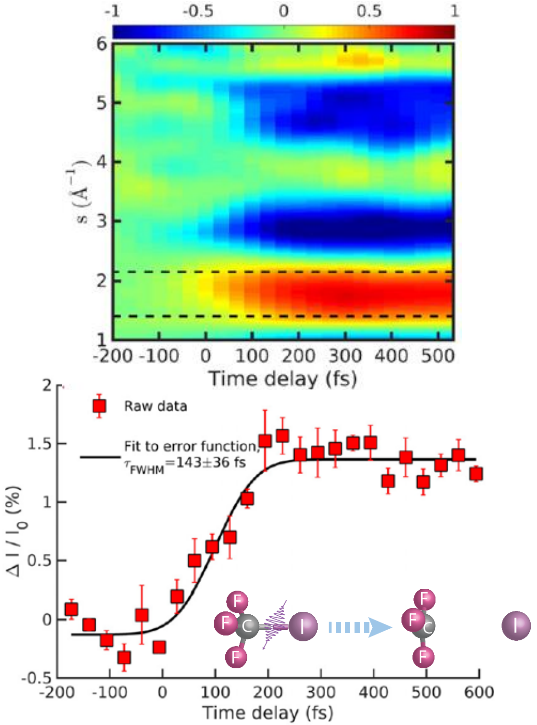
## Rotational revival of $N_2$ molecule




**Demonstration of gas-phase MeV UED, 250 fs**

J. Yang, *et al. Nature Comm*. **7**, 11232 (2016).

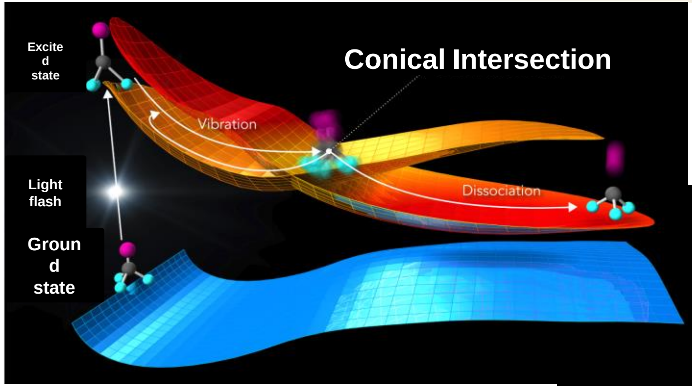
## $2^{nd}$ gen. gas-phase MeV UED

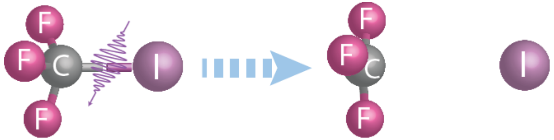



**< 150 fs time resolution**

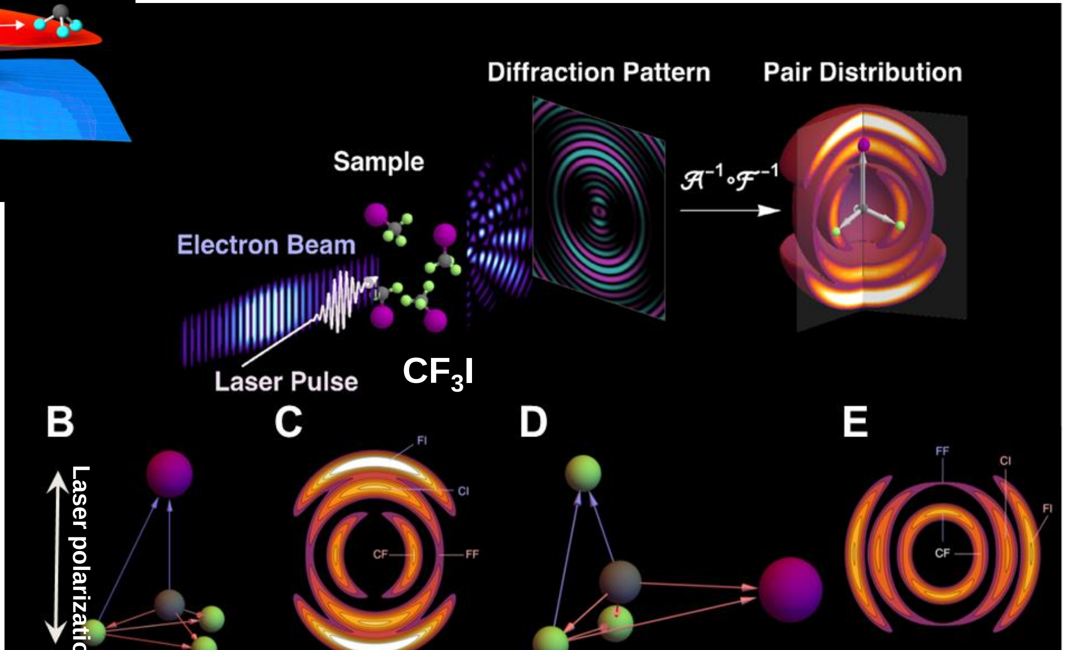
X. Shen, *et al.*, *Struct. Dyn*. **6**, 054305 (2019)

# Gas phase MeV UED



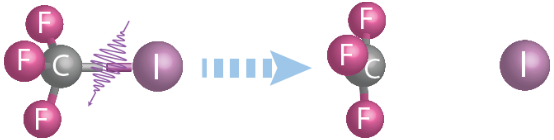



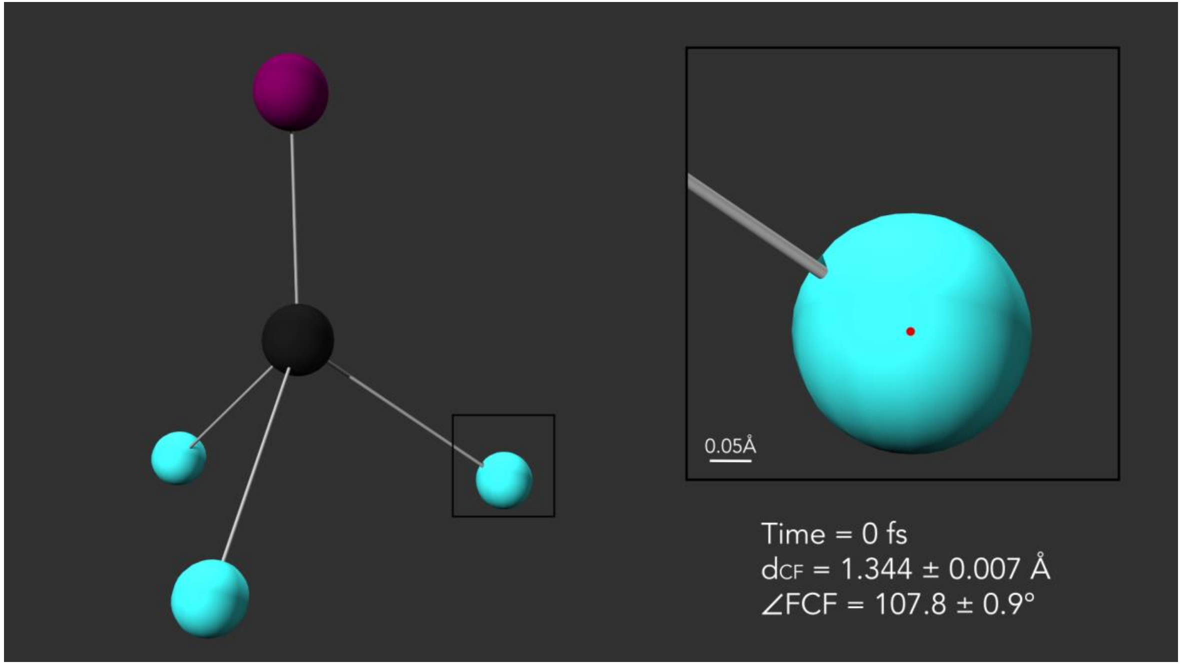

- $CF_3I$ photodissociation
- Conical interaction resolved




J. Yang, *et al.*, *Science* **361**, 64

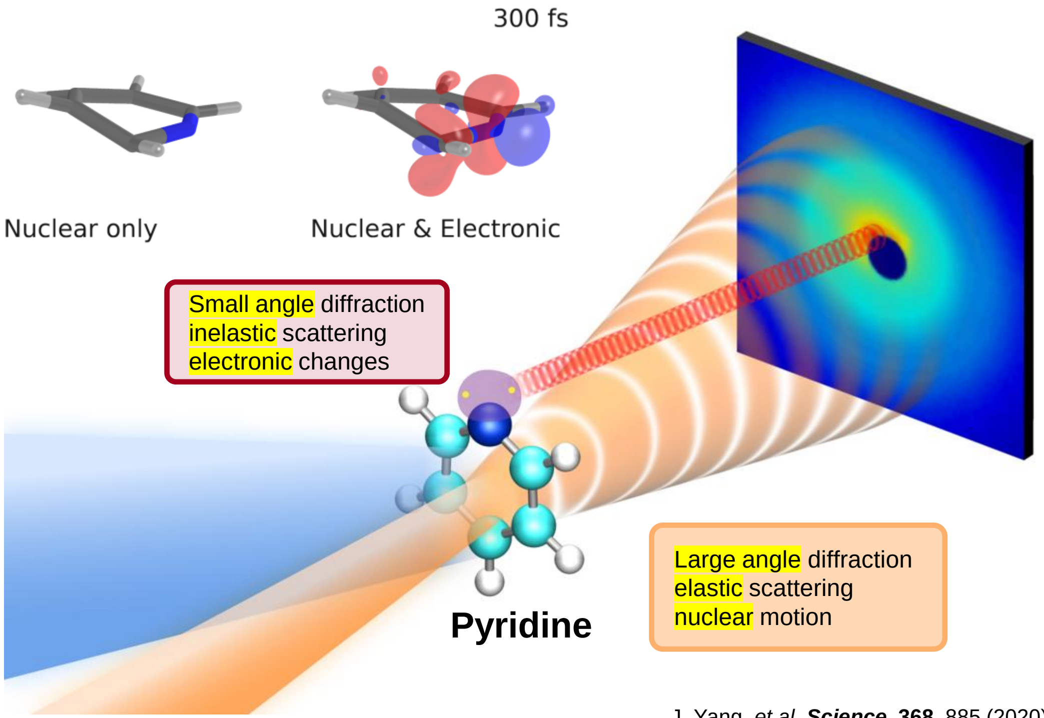
# $CF_3I$ photodissociation dynamics



# Gas phase MeV UED

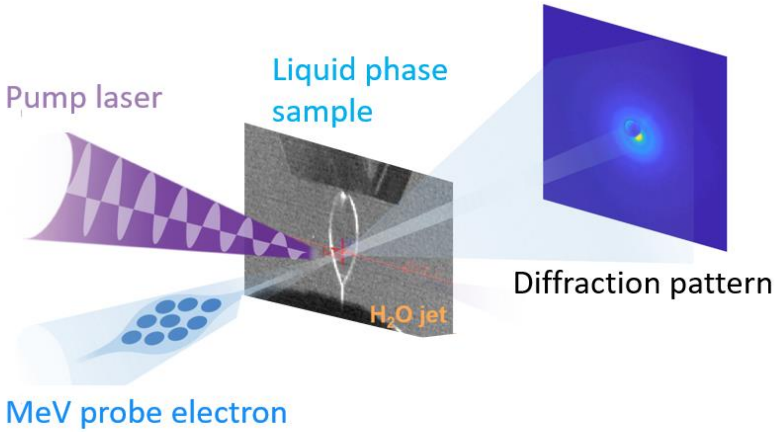
## Simultaneous capture of nuclear and electronic dynamics

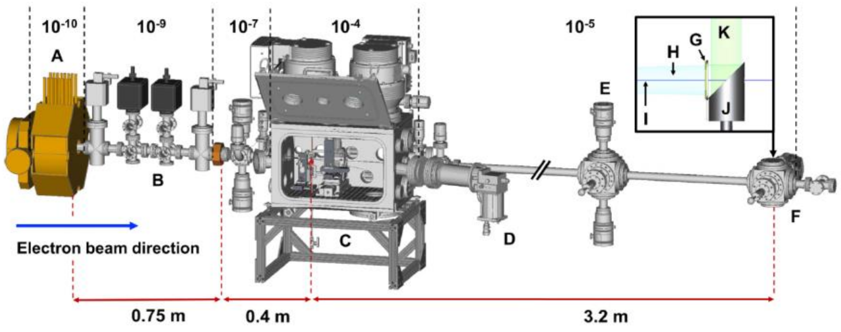


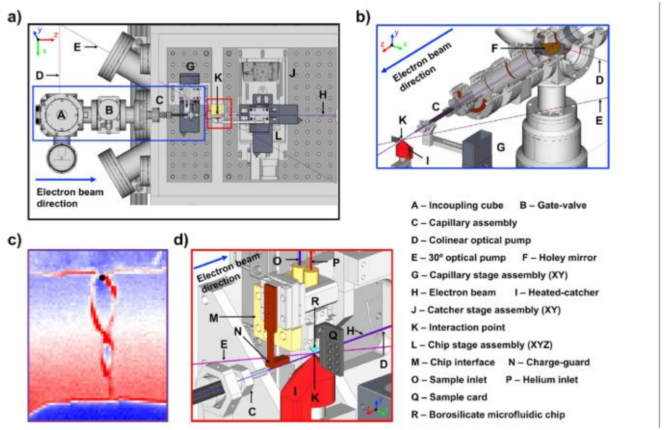

J. Yang, *et al.* ***Science.* 368,** 885 (2020)

# Liquid phase MeV UED

- Opportunities
  - Liquid solution is natural environment for chemis critical to life
- MeV electrons
  - High time resolution (< 150 fs)
  - High q range (12 $Å^{-1}$)
  - Large penetration depth (100 nm)
- Challenges
  - 6 orders of magnitude isolation of vacuum



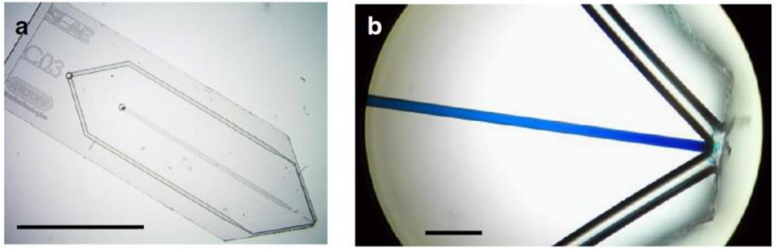



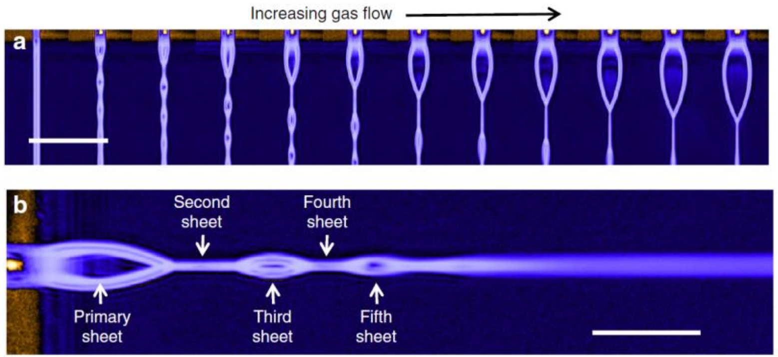




J. P. F. Nunes, *et al.*, *Struct. Dyn*. **7**, 024301 (2020)

# Liquid phase MeV UED

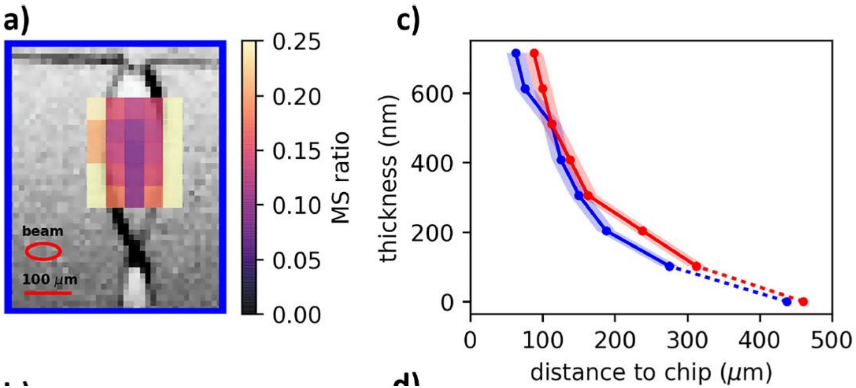
- Microfluid gas-dynamics nozzle adapted




*J.D. Koralek, *et al., Nat. Comm*. **9**, 1353 (2018)

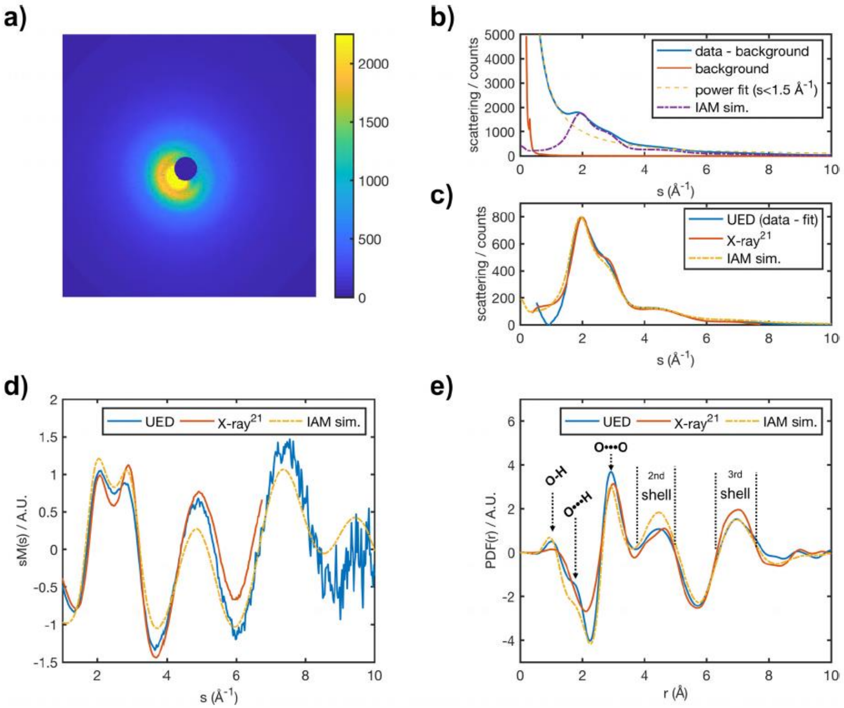
- Measure liquid jet thickness using interferometric imaging
  - < 100 nm region
- Measure e beam transmission at various locations
  - < 10% multiple scattering at thin region

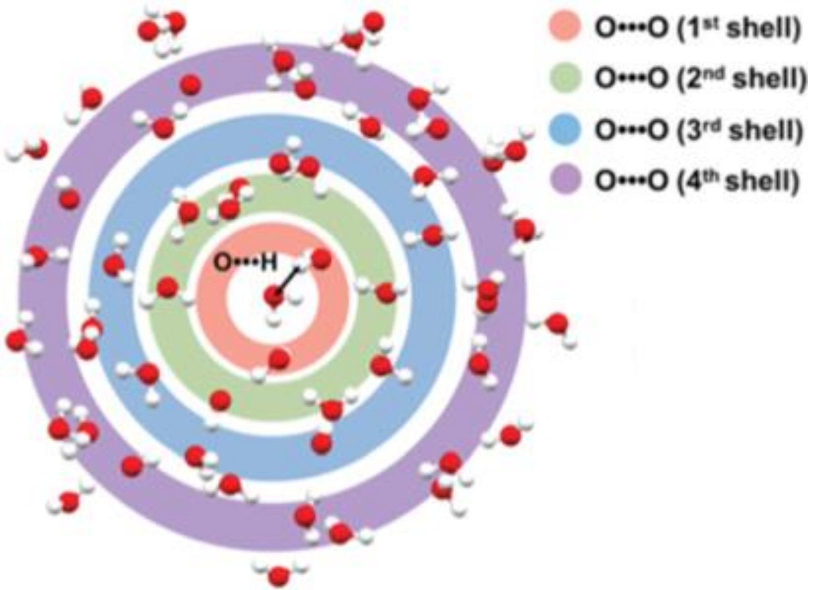



J. P. F. Nunes, *et al., Struct. Dyn*. **7**, 024301 (2020)

# Liquid phase MeV UED

Hydrogen bond resolved by MeV UED



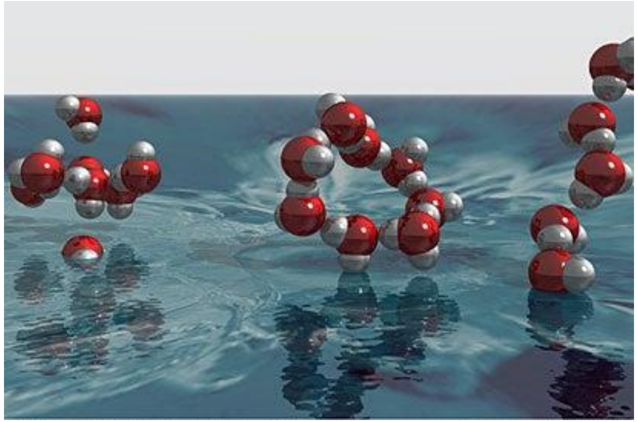



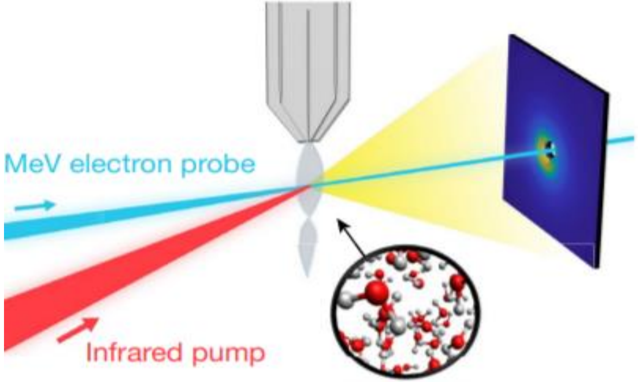

J. P. F. Nunes, *et al., Struct. Dyn*. **7**, 024301 (2020)

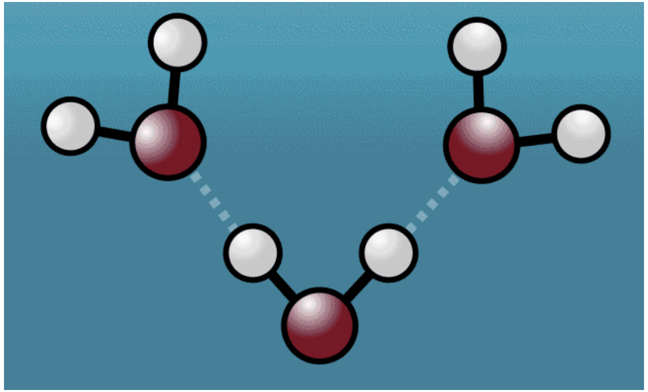
J. Yang *et al.*, *Phys. Chem. Chem. Phys.* **23**, 1308–1316 (2021).

# Ultrafast hydrogen bond strengthening in liquid water

Water
- Most abundant but least understood in nature
- Most dense at 39 deg F, anomalous compared to most liquids
- unusually high surface tension
- large capacity
- Ultrafast hydrogen bond motion captured by MeV UED





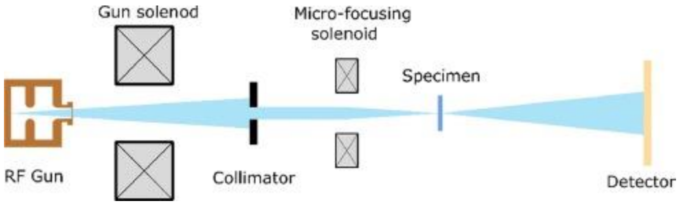



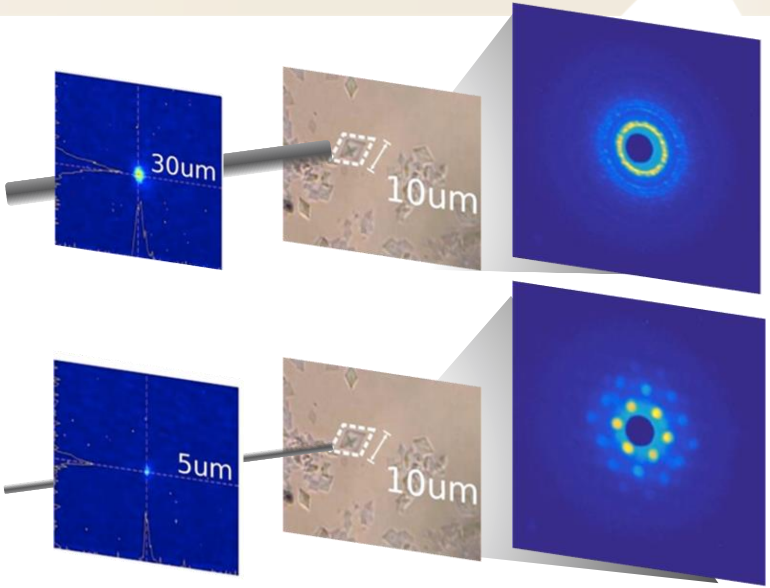
J. Yang *et al.*, *Nature*. **596**, 531–535 (2021).

# Outline

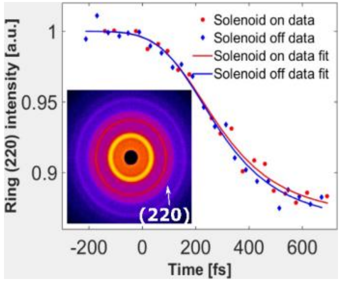
- Introduction
- SLAC MeV UED
- Science highlights
- R&Ds

# Femtosecond MeV electron microdiffraction




- **30 μm rms** electron beam size on **10 μm** Paraffin ($C_{44}H_{90}$) crystal, **0.17 $Å^{-1}$** reciprocal space resolution
- **5 μm rms** electron beam size on **10 μm** Paraffin ($C_{44}H_{90}$) crystal, **0.63 $Å^{-1}$** reciprocal space resolution
- Maintain **~100 fs rms** temporal resolution
- Optimization of emittance
- Opportunities to explore ultrafast structural dynamics over **localized crystalline area**

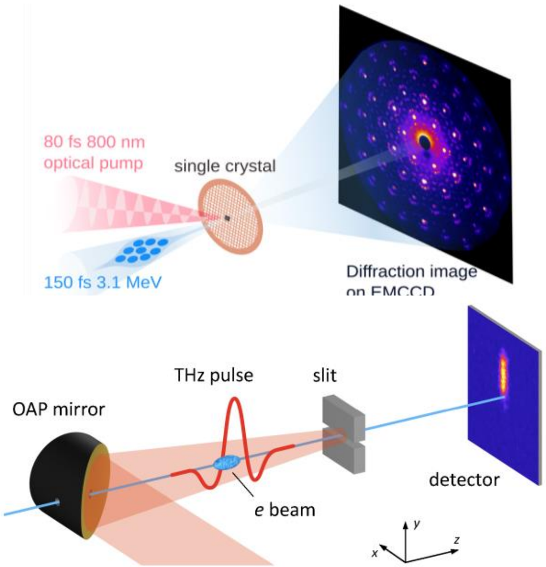



X. Shen *et al.*, *Ultramicroscopy* **184**, 172 (2018)

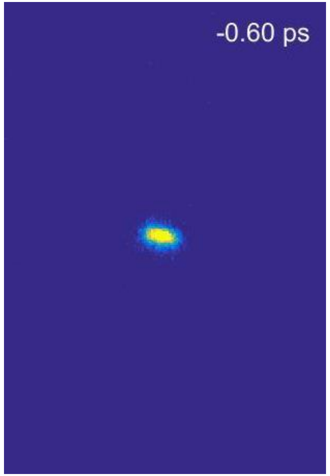
# Electron beam characterization with THz streaking

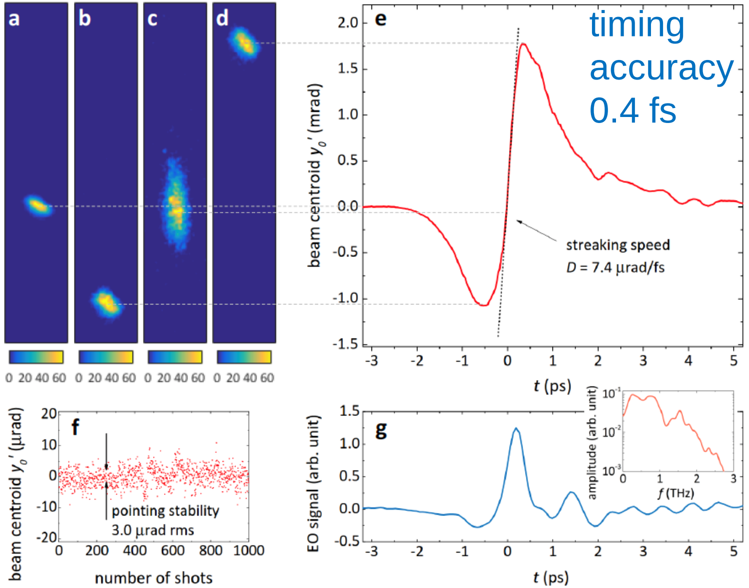
UED temporal resolution

$$\tau = \sqrt{\tau_{laser}^2 + \tau_{electron}^2 + \tau_{VM}^2 + \tau_{TOA}^2}$$




**3.1 MeV electrons, 50 um gap, 100 um thick slit**

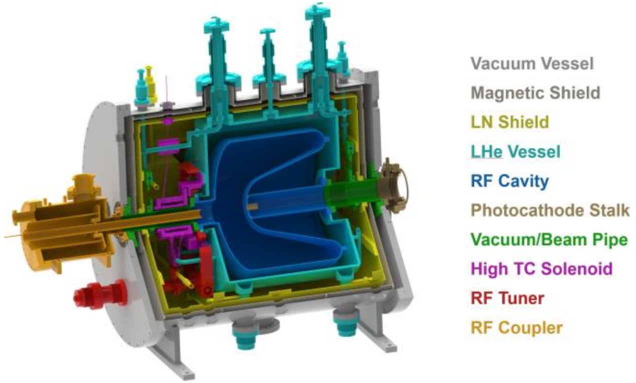


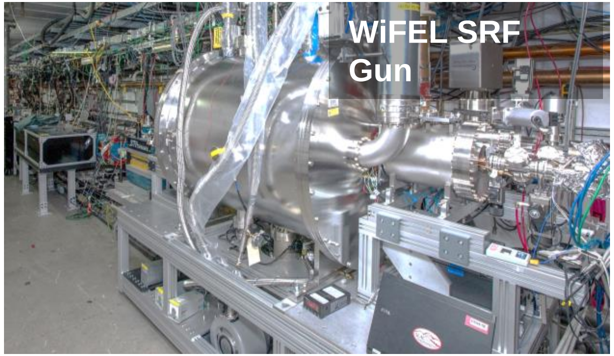




*R. K. Li, M. C. Hoffmann, E. A. Nanni et al., Phys. Rev. Accel. Beams* **22**, 012803 (2019).

# VHF SRF gun for MHz UED & single-shot UEM

- High rep-rate:
  - up to 200 MHz
- High RF stability:
  - towards $10^{-5}$ amplitude and 10 fs phase stability
- High acceleration gradient:
  - > 25 MV/m high peak beam brightness
- High beam energy:
  - 4 MeV, space charge effect suppression
- High flexibility:
  - MHz UED & single-shot UEM
- Synergy with LCLS-II HE




Courtesy of Xijie Wang

# Acknowledgement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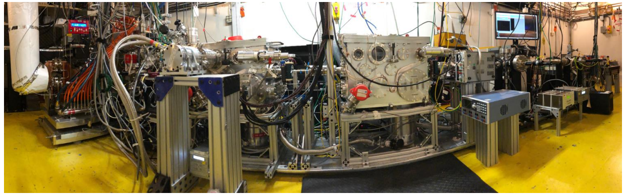
SLAC UED/UEM Initiative Program Development Funds (SLAC program development and AD program development), and Laboratory Directed Research & Development (LDRD) fund.

The technical support provided by SLAC Accelerator Directorate, Technology Innovation Directorate, and LCLS is grateful acknowledged

# Acknowledgement

# Thank you for your attention!

## SLAC MeV UED



| | |
|---|---|
| **Q range (with 2$\pi$)** | 12 Å$^{-1}$ |
| **Q res. (FWHM)** | 0.17 Å$^{-1}$ |
| **Time res. (FWHM)** | < 150 fs |
| **Stability** | NONSTOP >5 days |