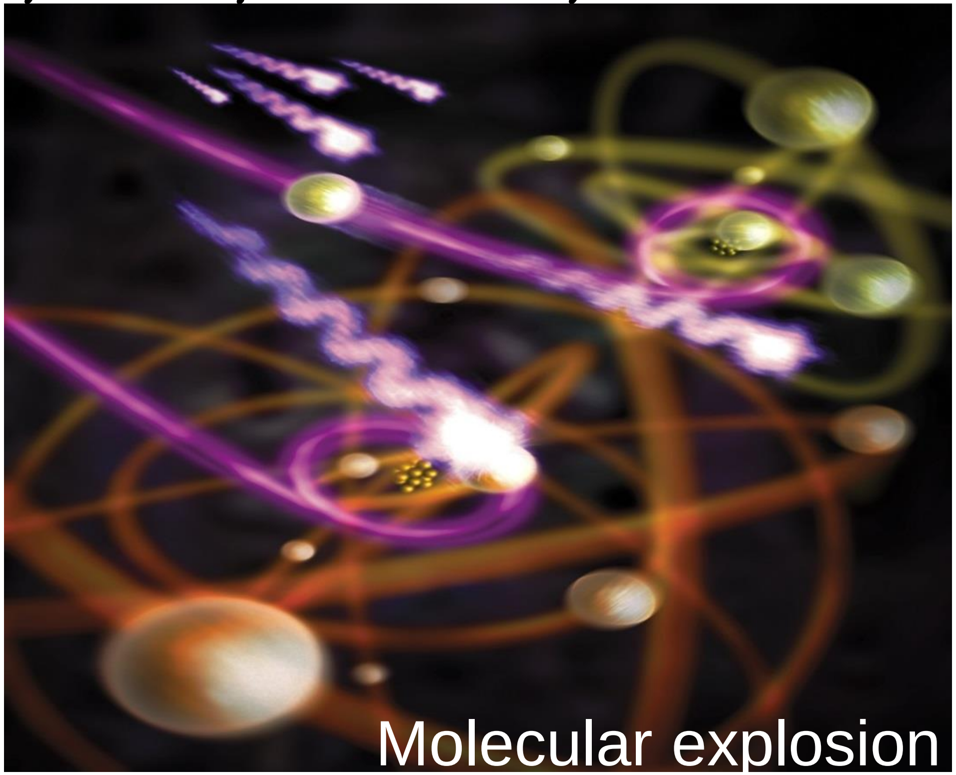
X-Ray Induced Dynamics in Fullerenes using FELs

Nobel Symposium on FEL research, Sigtunahöjden 2015

Nora Berrah,
Physics Dept, University of Connecticut



Funded by the Department of Energy, Office of Science BES

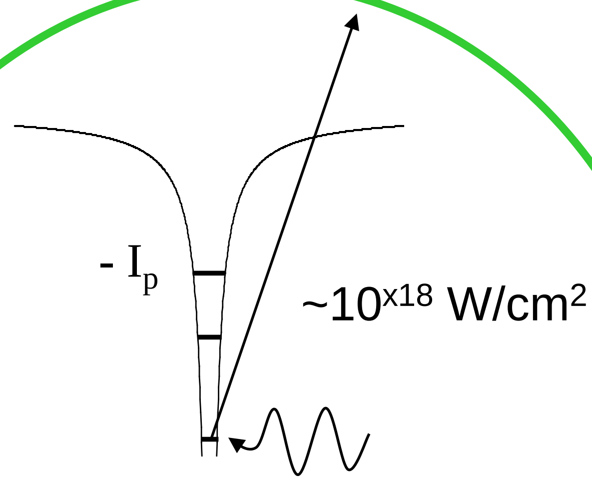
X-Ray Induced Molecular Dynamics

What are the Fundamental Inner Working of Molecular Systems?

How does the FEL energy flow, through all transient stages of a system, from the initial state to the final product?

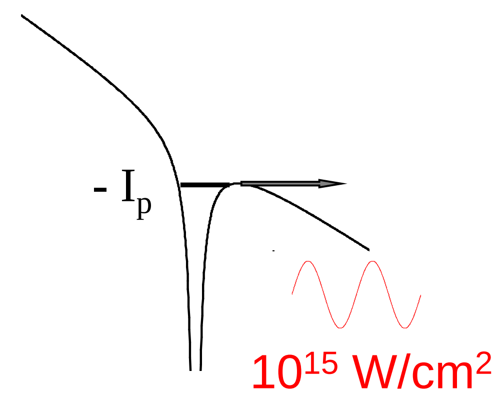
Ultraintense and Ultrafast X-FEL & IR Sources: Different Ionization Processes

X-FELaser:
Highly ionizing source



- Keldysh parameter γ >>1
- **Angstrom wavelength**
- **Direct multiphoton ionisation**
- **Secondary processes**
- Ponderomotive E. 10 meV

IR Laser:
Low frequency regime

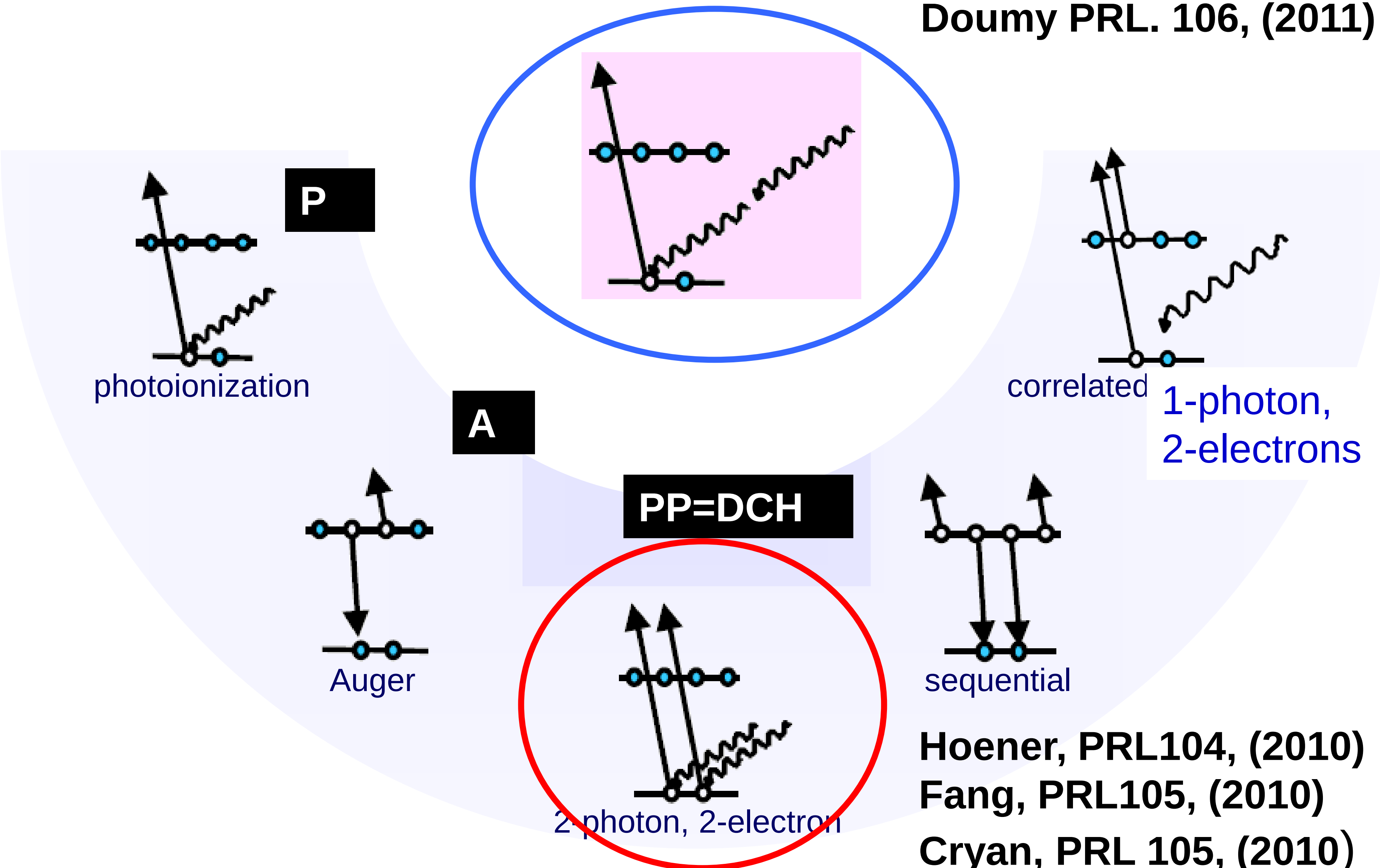


- Keldysh parameter γ <<1
- **Tunneling / over the barrier ionisation**
- Ponderomotive Energy 10 – 100 eV

$$\gamma \equiv \frac{\text{Optical Frequency}}{\text{Tunneling Frequency}} = (I_p/2U_p)^{1/2} \propto \lambda^{-1};\ U_p = I/4\omega^2 \ \text{(au)}$$

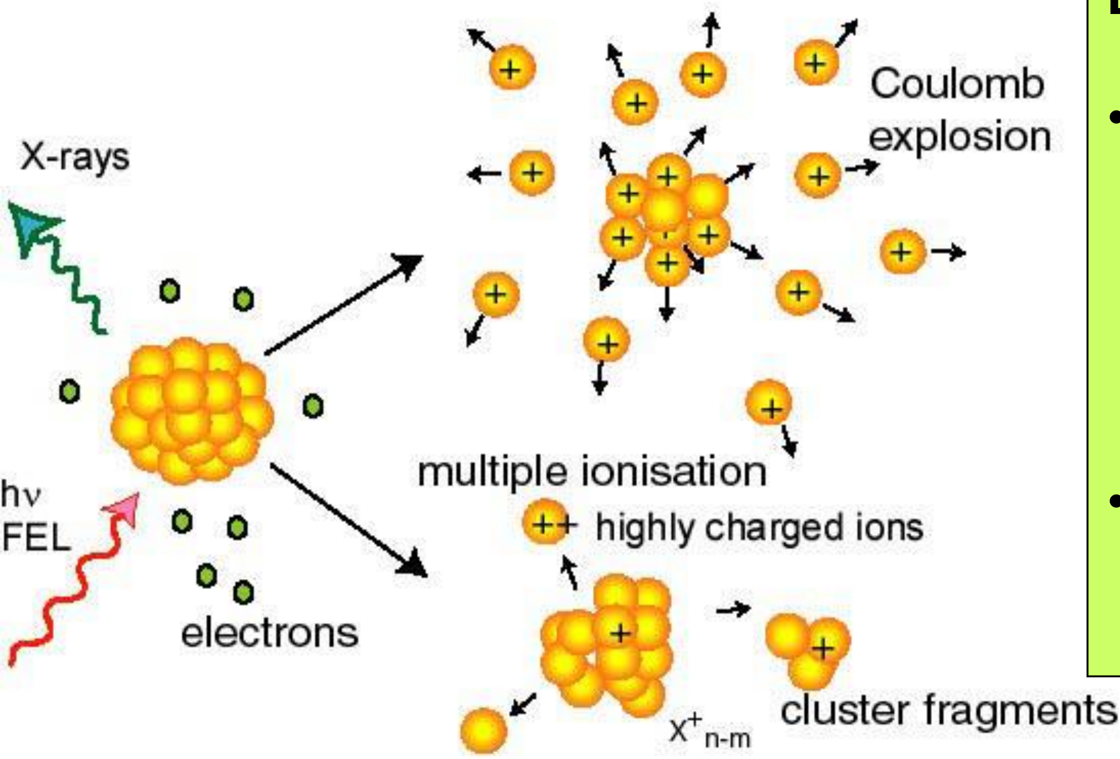
Multiphoton Ionization with X-Ray Absorption: Possible Processes @ the Atomic Level

Doumy PRL. 106, (2011)



Hoener, PRL104, (2010)
Fang, PRL105, (2010)
Cryan, PRL 105, (2010)

C_{60} fs Dynamics : A Model System for Complex Molecules



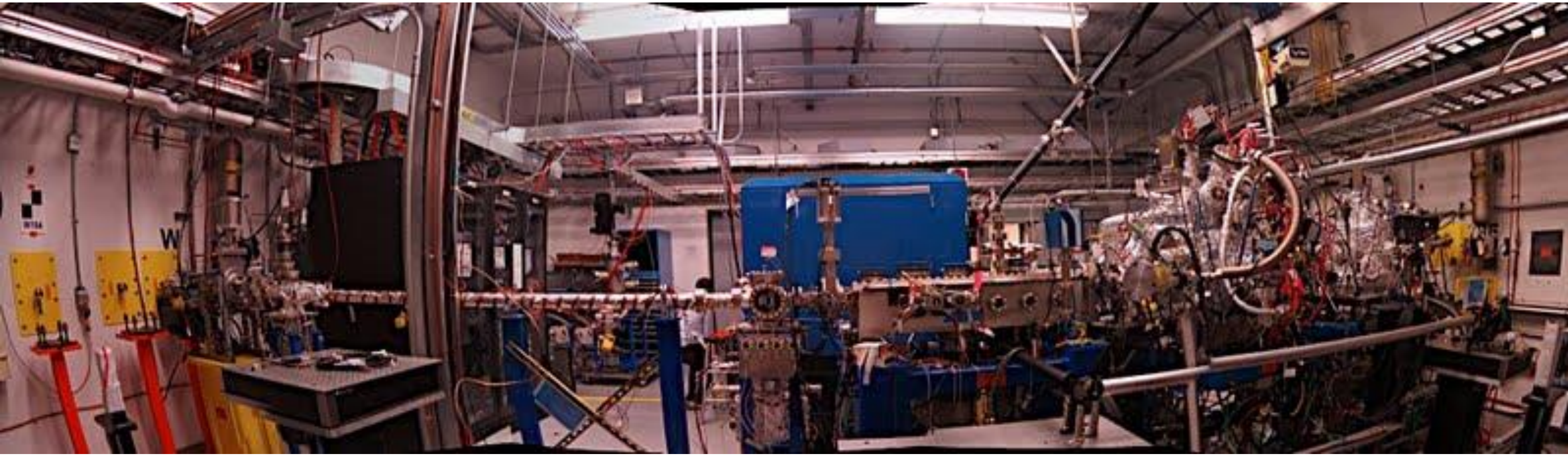
Driving questions:

- **Quantitative Understanding of fs Molecular Dynamics Induced by Intense X-ray Exposure?**
- **Testing Molecular Dynamics Models on strongly bonded systems; C-C bonds?**

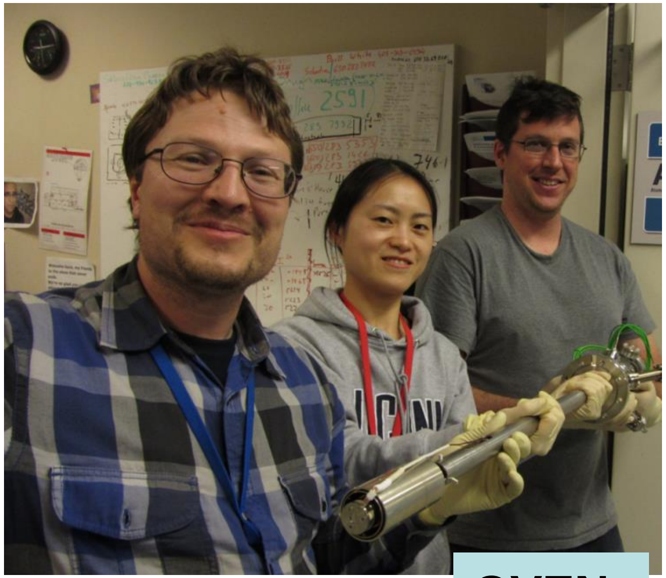
***Findings give insight on*: 1) fs molecular dynamics 2) Matter under extreme conditions, 3) Radiation damage of bio-molecules during imaging with intense x-ray exposure.**

AMO Hutch @ LCLS

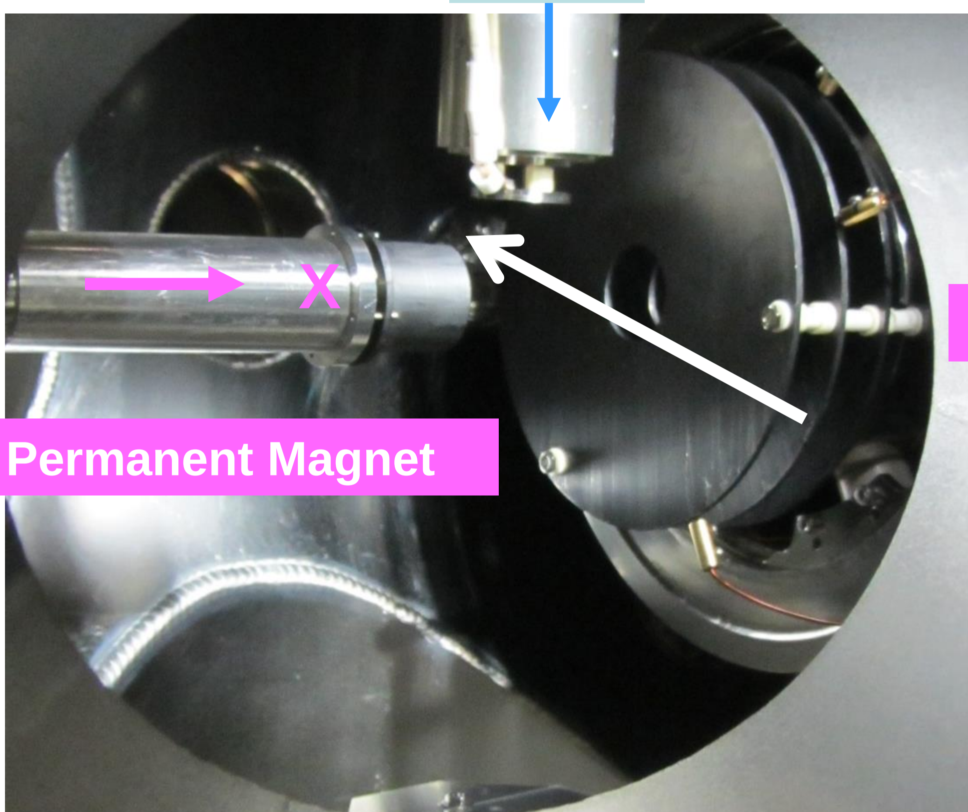
Berrah & Bucksbaum Scientific American, **310**, 64, 2014



Oven in Chamber:10^{-10} T

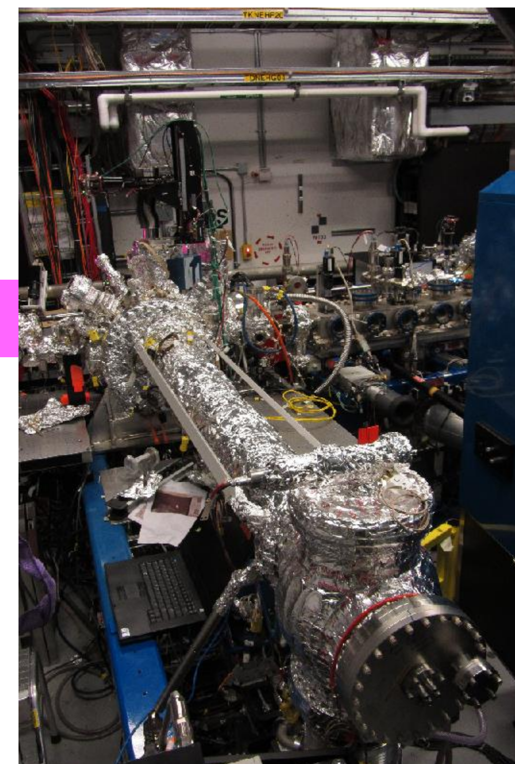


OVEN

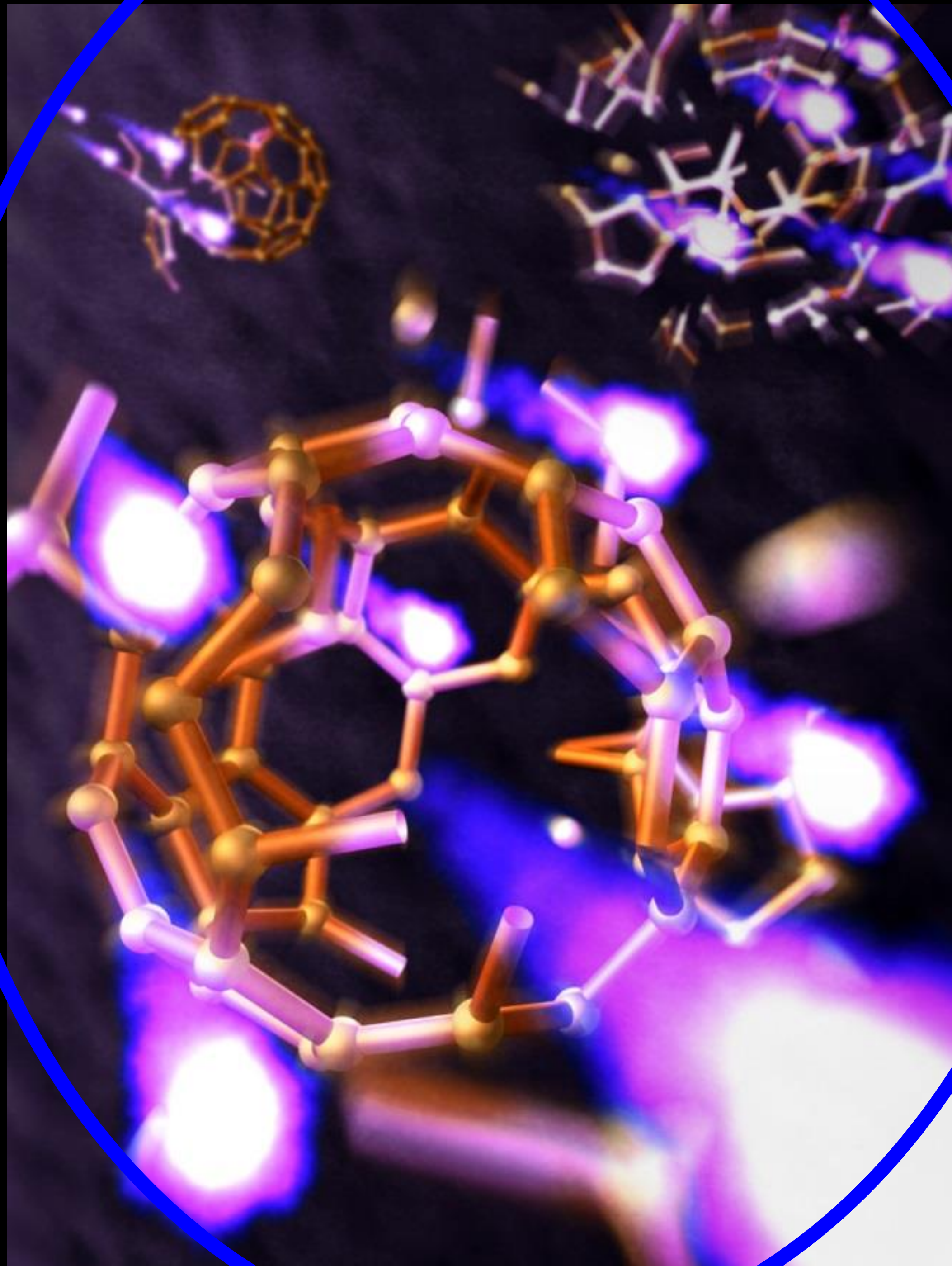


Permanent Magnet

Spectrometer

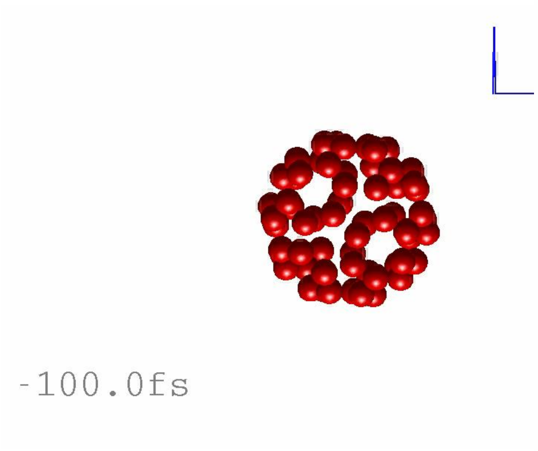


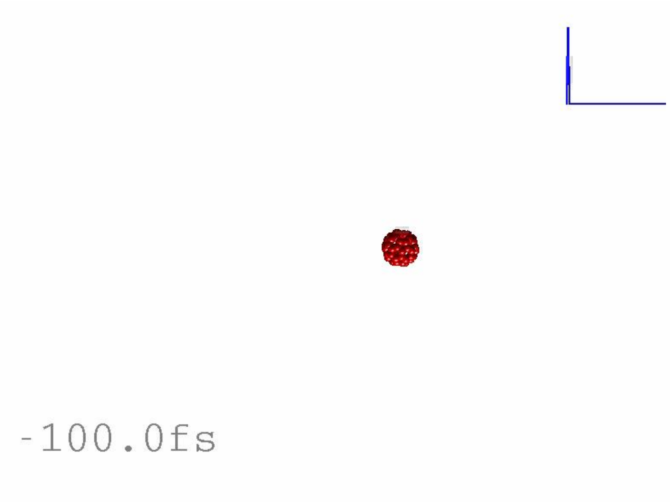
Multiple Sequential P & A



180 X-Ray Photon Absorbed
87 keV Energy Tranfer

Exploding C_{60}



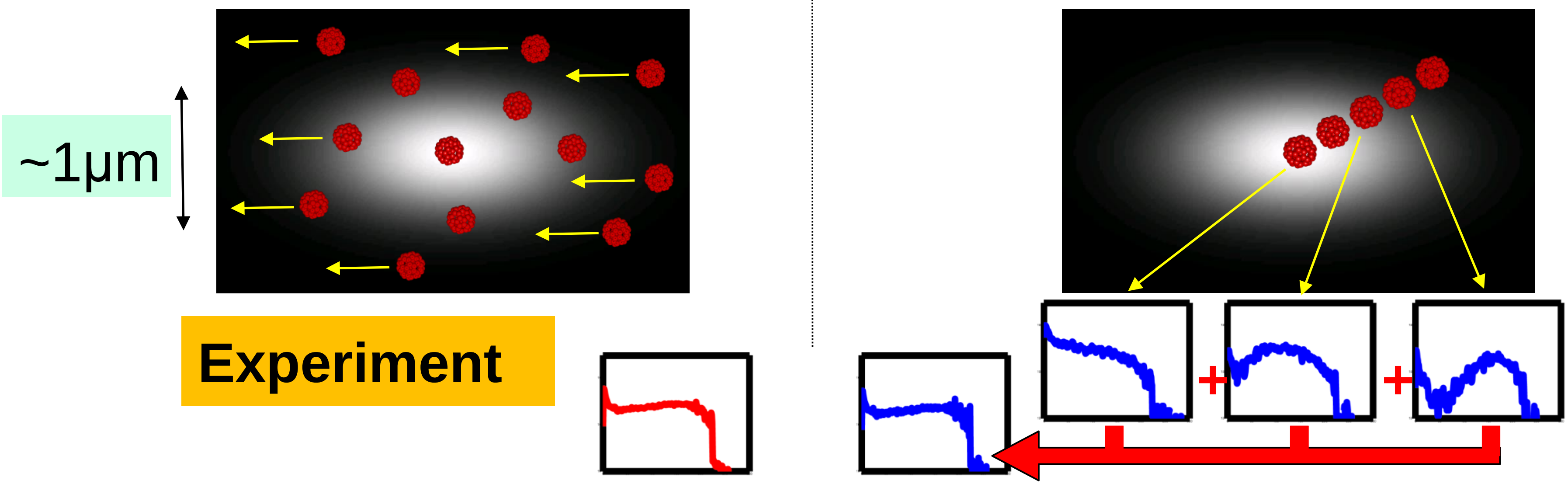


Low fluence **Mid fluence** **High fluence**

Modeling: Challenging!

- **Large number of particles** (atoms + electrons)
- **Initial condition**: system of neutral C atoms + Molecular Dynamics (MD)
- **System is excited** (large number of ionizations)
- **Long time propagation; >ps** (typical time-step ~as)

- **Spatial intensity profile of the beam** ⟶ **volume integrated signal**



Experiment vs. Theory

Theory

Jurek, Son, Santra,CFEL DESY

Modeling tool

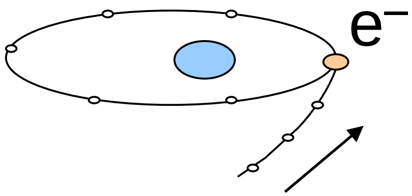
Real space dynamics:

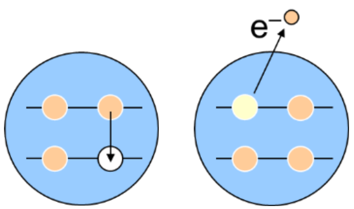
- Atoms/ions and quasi-free electrons: classical particles/Newtonian mechanics. BUT Rates and Cross Sections; Quantum-Mechanically.
- Atoms held together by classical force fields. Charges interact Coulomb forces, Non-rel. equation of motion

Experiment identified Key processes required in the Model:

Effects of the Molecular Environment

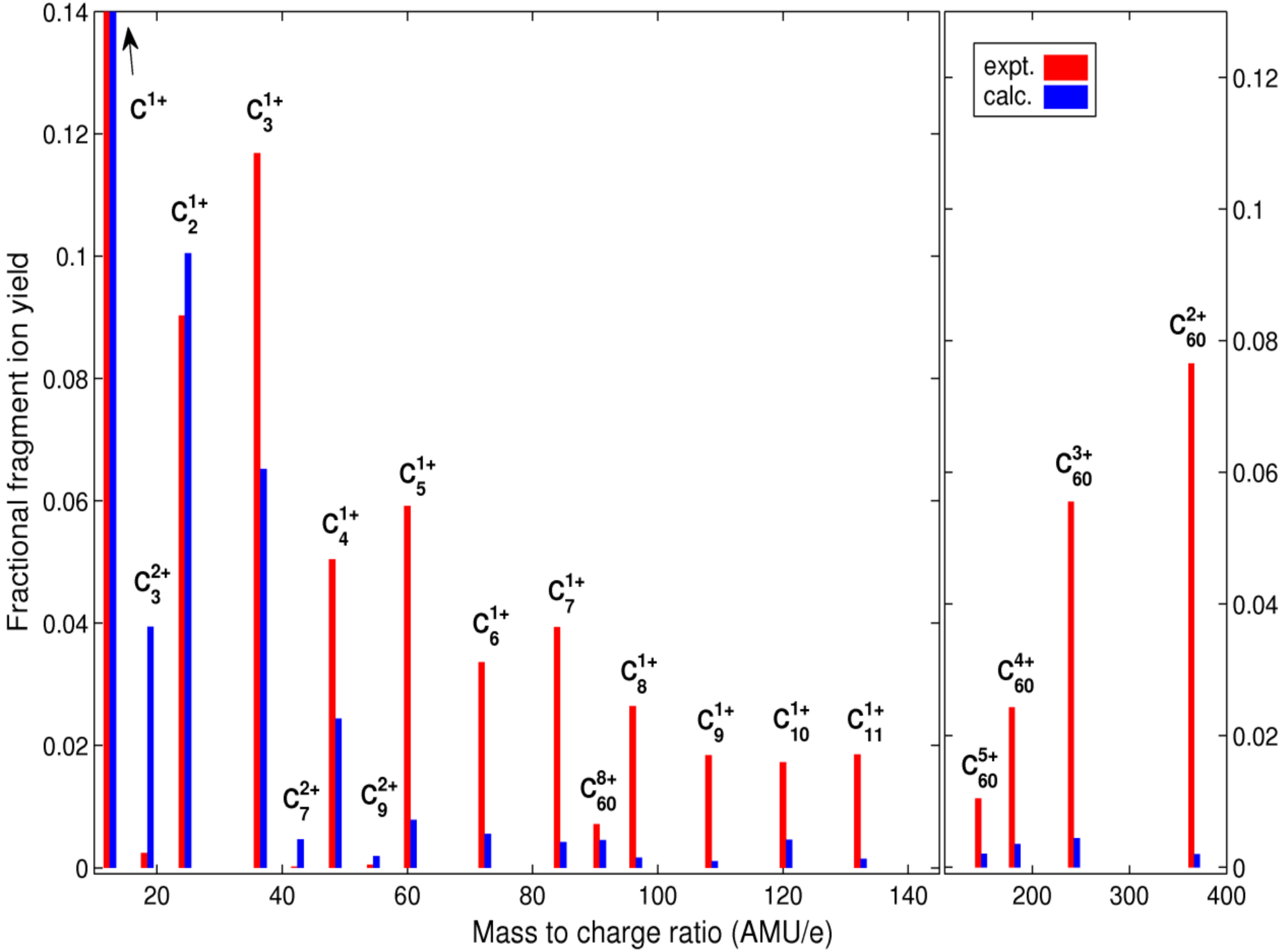
- ✓ ***Chemical bonds*: classical force fields**
- ✓ **Molecular Auger process: atom and neighboring sites are involved**
- ✓ **Recombination of e- with ions**



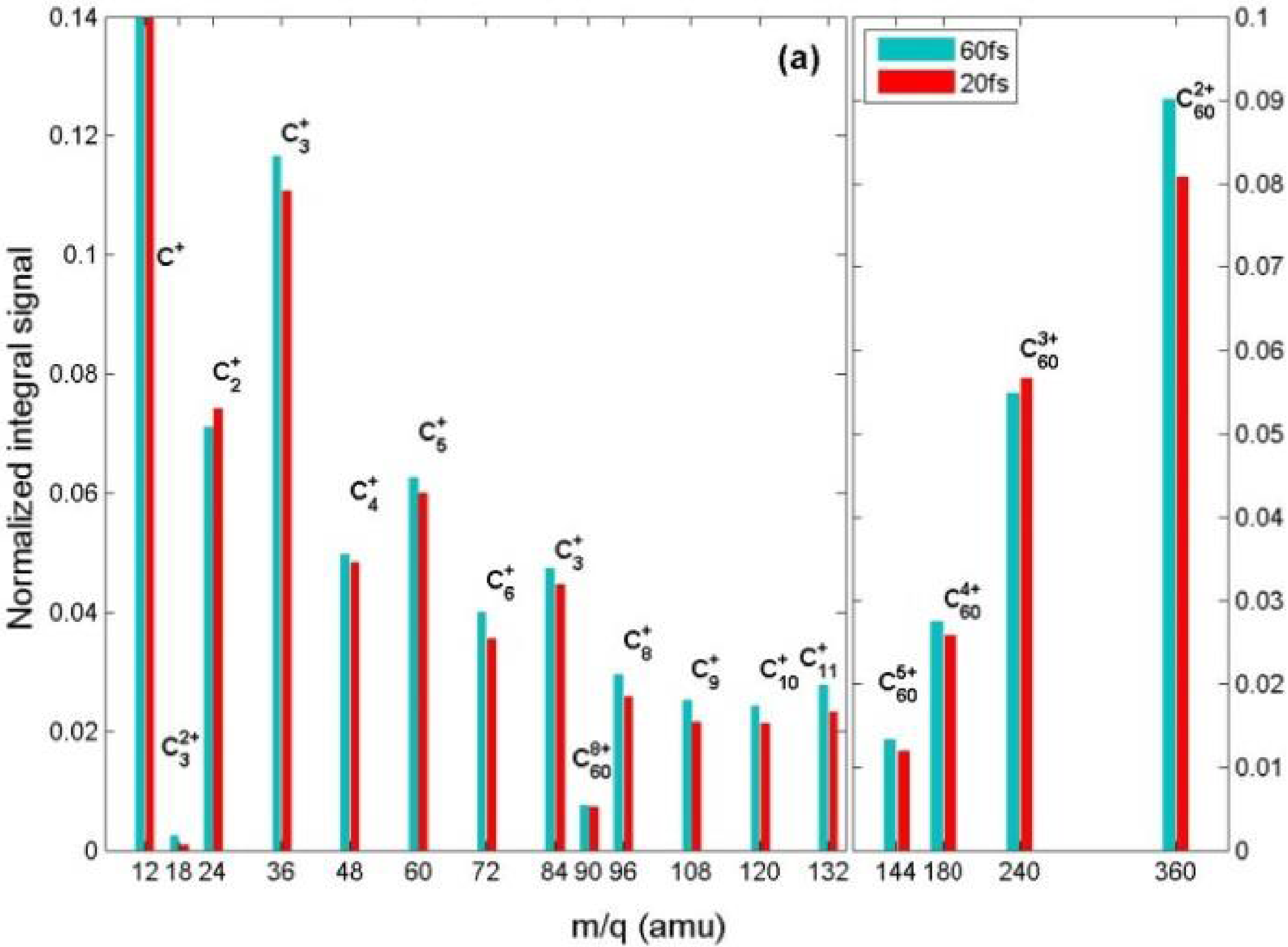


Jurek et al., Eur. Phys. J. D **29**, 217, 2004

Sequential Multi-Photon Ionization of C_{60} in Mid Fluence Region of X-FEL Beam: Molecular Fragments Ion Spectra

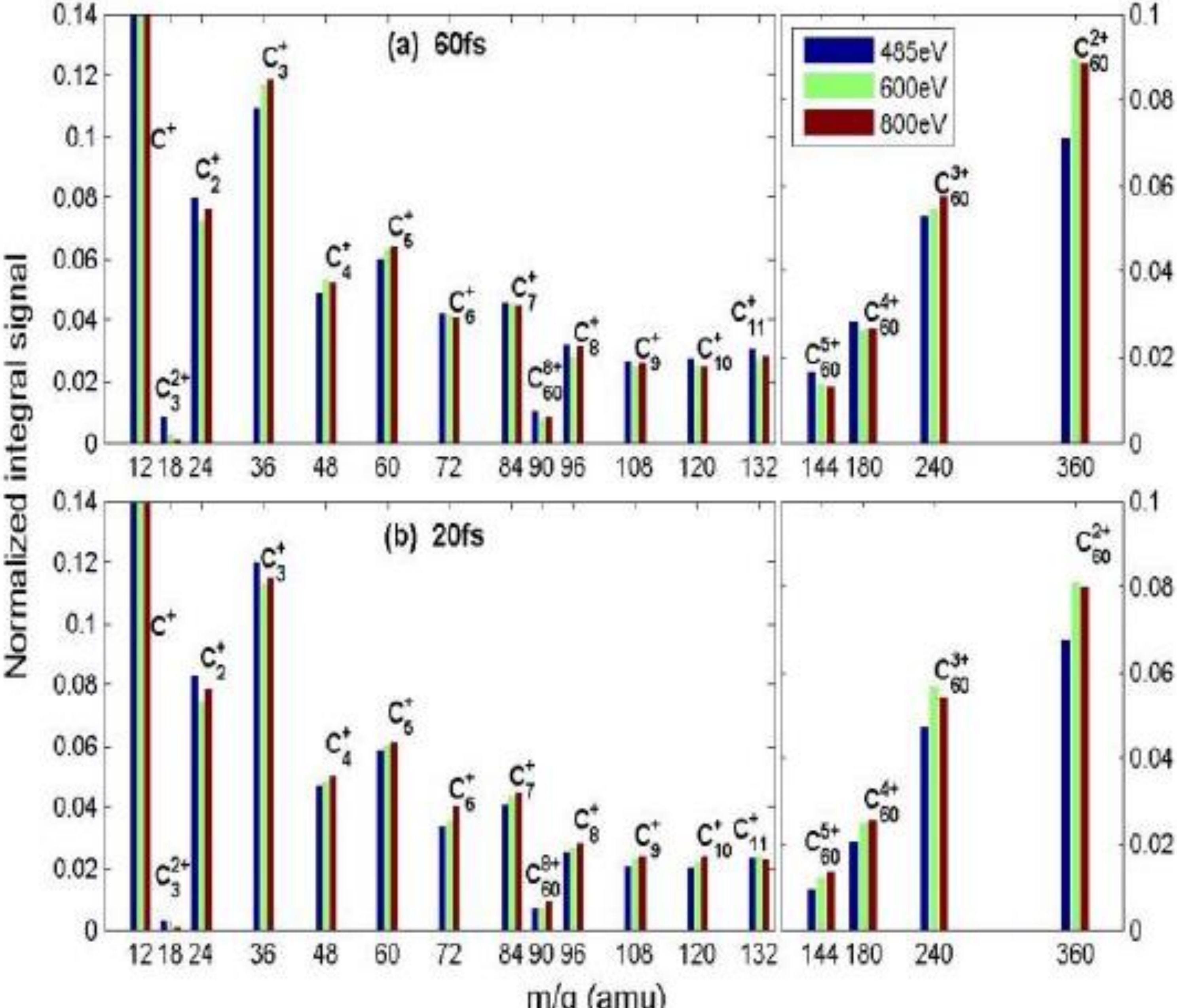


Photon energy=485 eV; Pulse duration= 90 fs; Pulse energy=0.61mJ.



Mid Fluence: hv=600 eV; pulse energy=0.61mJ. 60 fs (30fs); 20fs (13 fs).

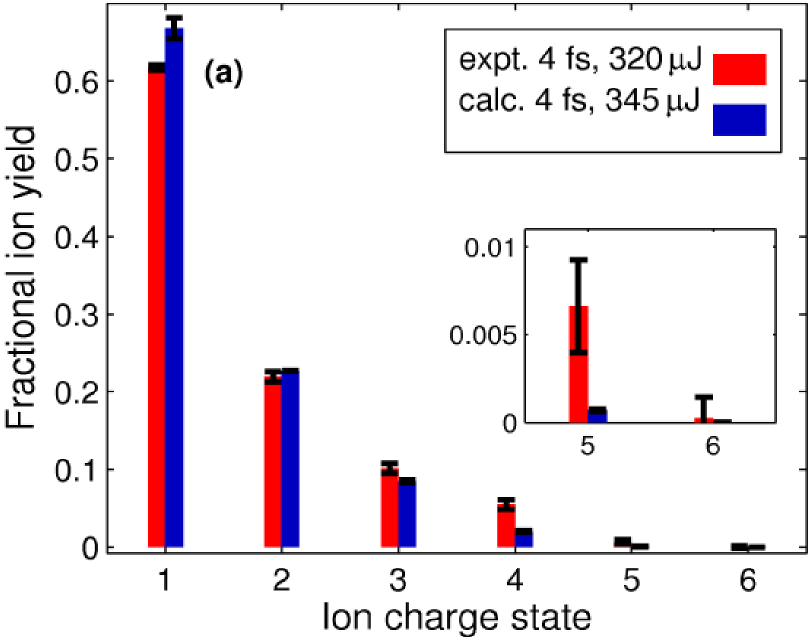
Berrah, Fang, Osipov,Jurek, Murphy, Santra, Faraday Discuss.,171, 471 **(2014)**

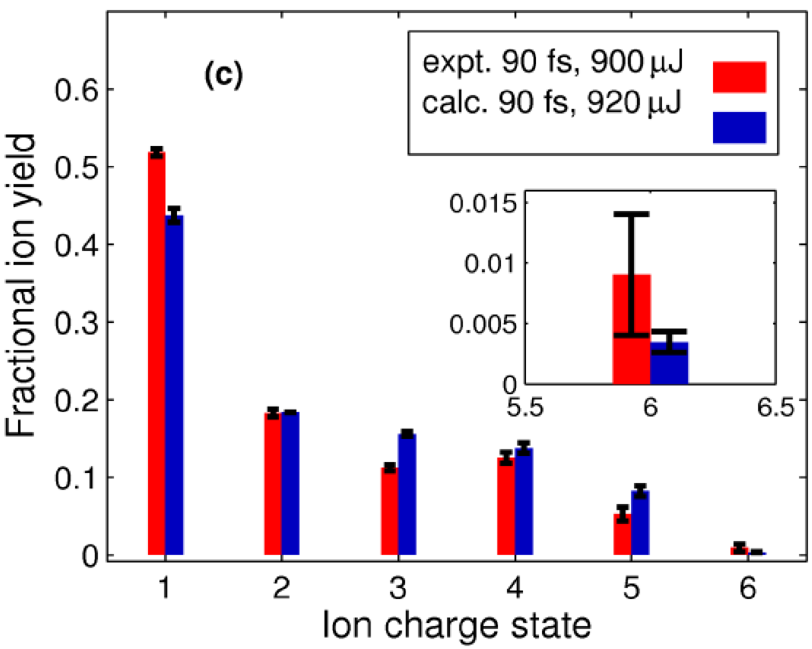


Mid Fluence

σ_{485} =18 Mb
σ_{600} = 11 Mb
σ_{800}= 4.9 Mb

Challenge: Need Characterization of FEL pulses





Central high fluence region: Comparison of C^{n+} states with model (hv=485 eV)

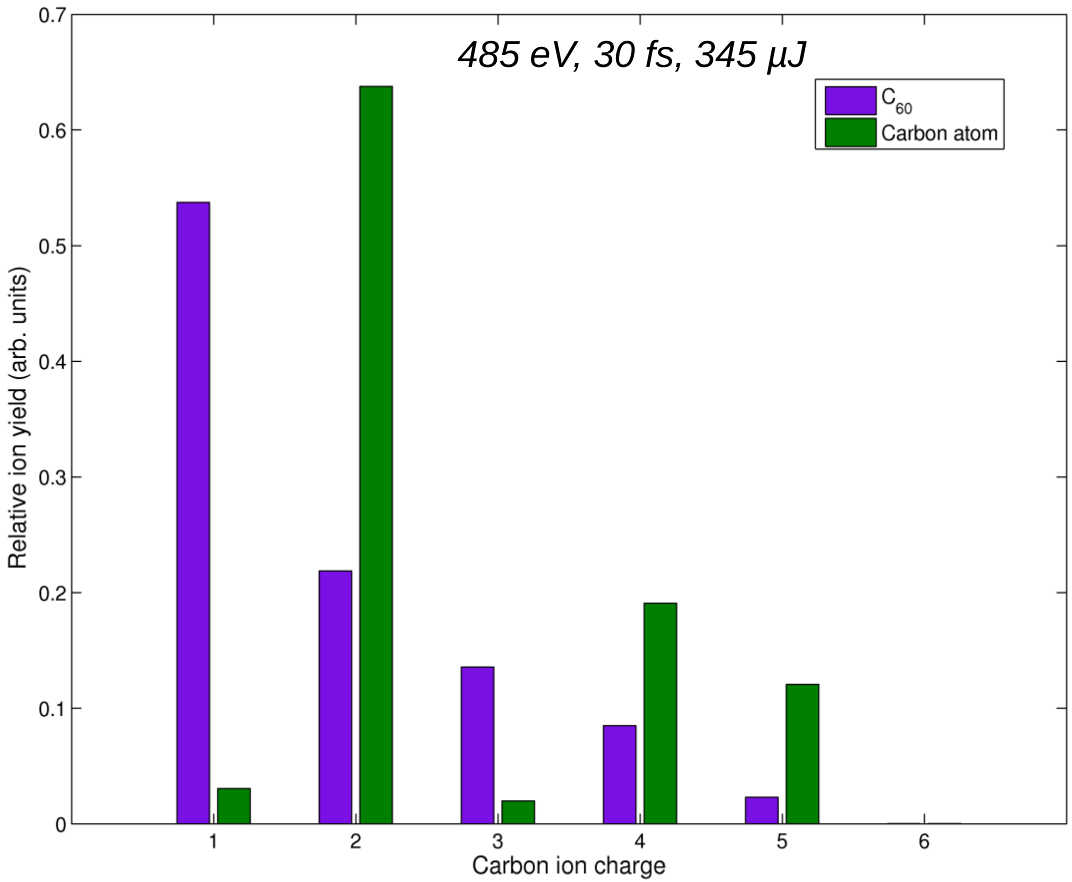
- ✓ **Yield for higher charge states decreases when we decrease the pulse duration BUT $C^{3}+$, $C^{4}+$!**

- ✓ **Model predicted initially MORE abundant charge states ⇨ strong recombination after the pulse ends.**

Theory:

Jurek, Son, Santra, CFEL DESY.

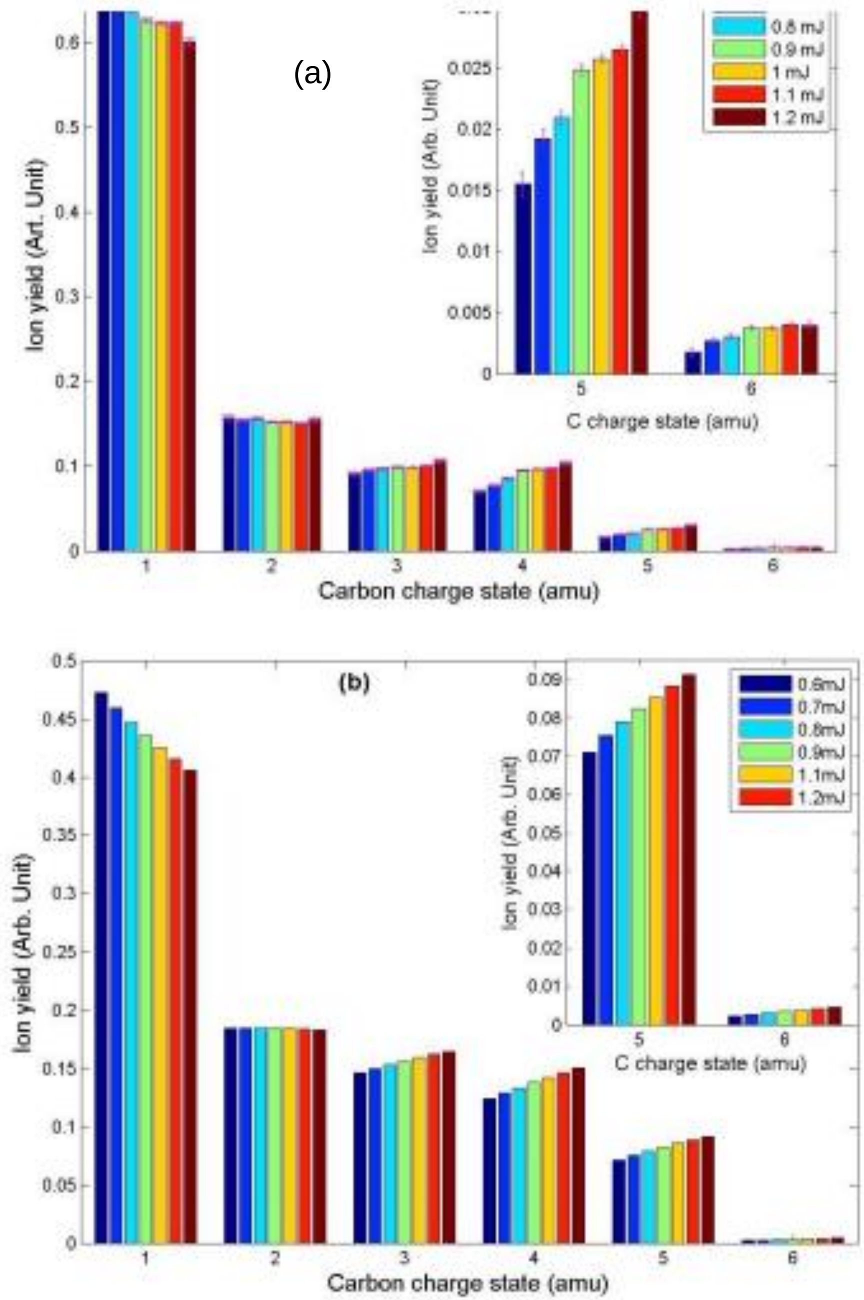
Importance of Molecular Effects?



- **Huge discrepancy in C^{1+} and C^{2+} model yield between C_{60} and C is a consequence of Atomic Auger (produces C^{2+} from C) and Molecular Auger effect (produces two C^{1+} ions from 2 C atoms in C_{60}**

- **Yield for C_{60} atomic fragments is strongly suppressed compared to ionization of isolated C atoms (recombination)**

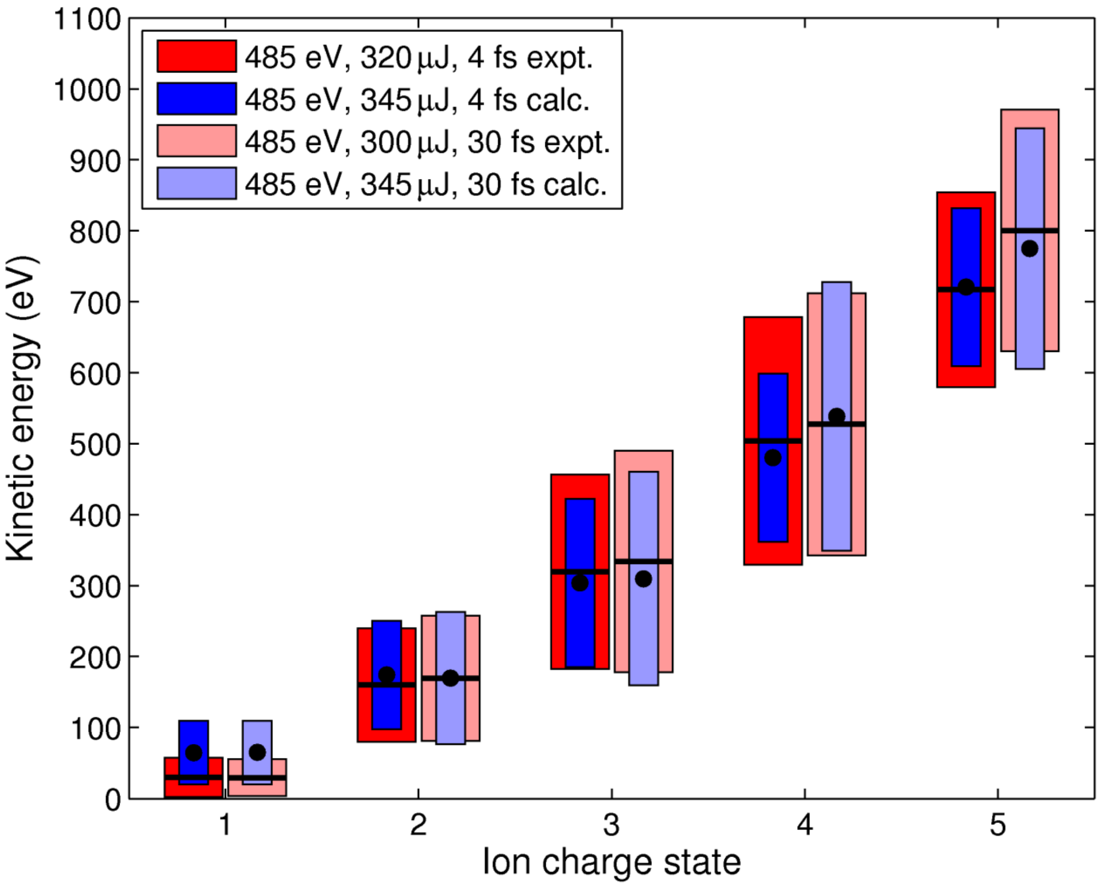
Murphy,Osipov,Jurek, Fang,Son, Avaldi,Bolognesi, Bostedt,Bozek, Coffee, Eland,Guehr,Farrell, Feifel, Frasinski,Glownia,Ha,Hoffmann,Kukk,McFarland, Mucke, Squibb,Ueda,Santra & Berrah **(Nature Communication** Nature Comm, **5**, 4281, (2014)



Carbon Ion Fragment Charge State Distribution Dependence on the FEL Pulse Energy

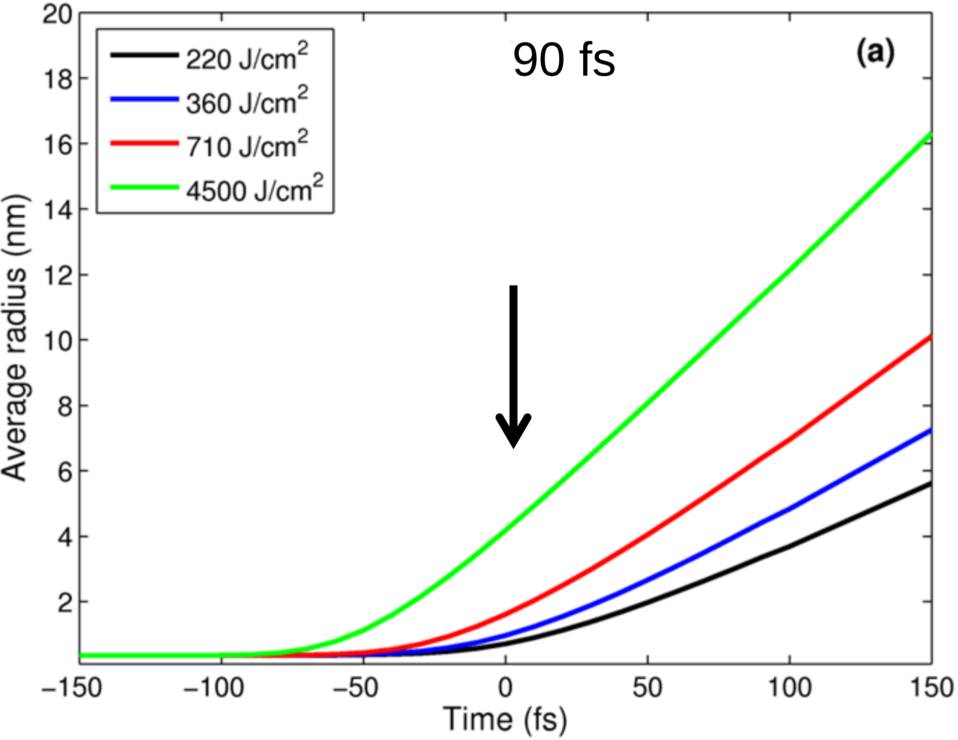
(a) Expts
(b) MD model

Nanoplasma characterization: Fragment Atomic C Ion Kinetic Energy (Central high-fluence region)



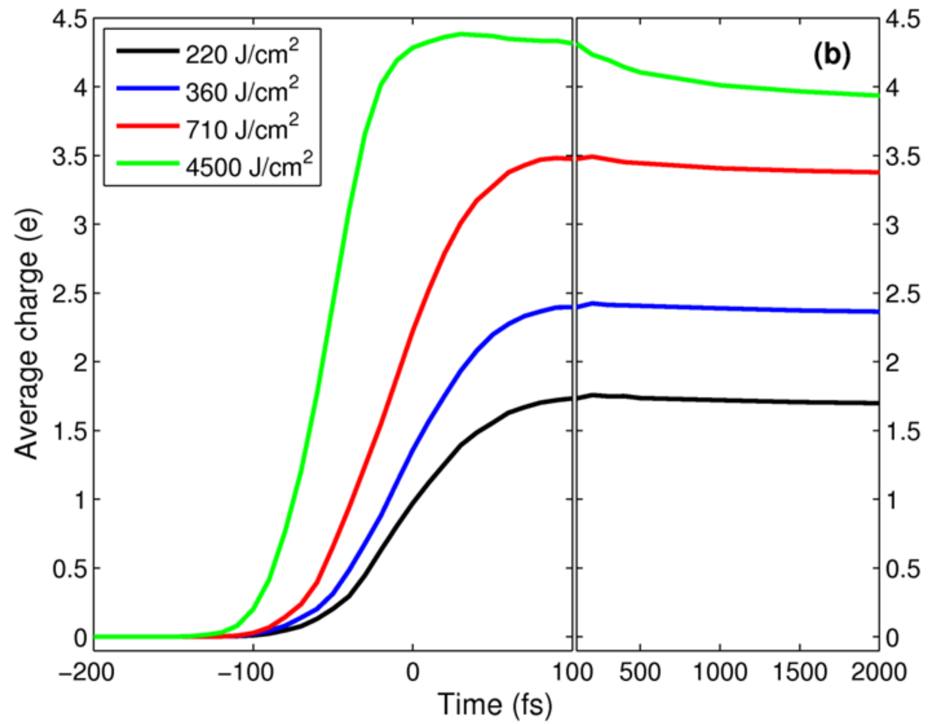
Quadratic Scaling of Mean Ion KE with C^{n+} Expansion is Coulombic.

Mean ion kinetic energy: **circles (experiment)** and **lines (simulation).**
RMS kinetic energy width: Height of each rectangle.



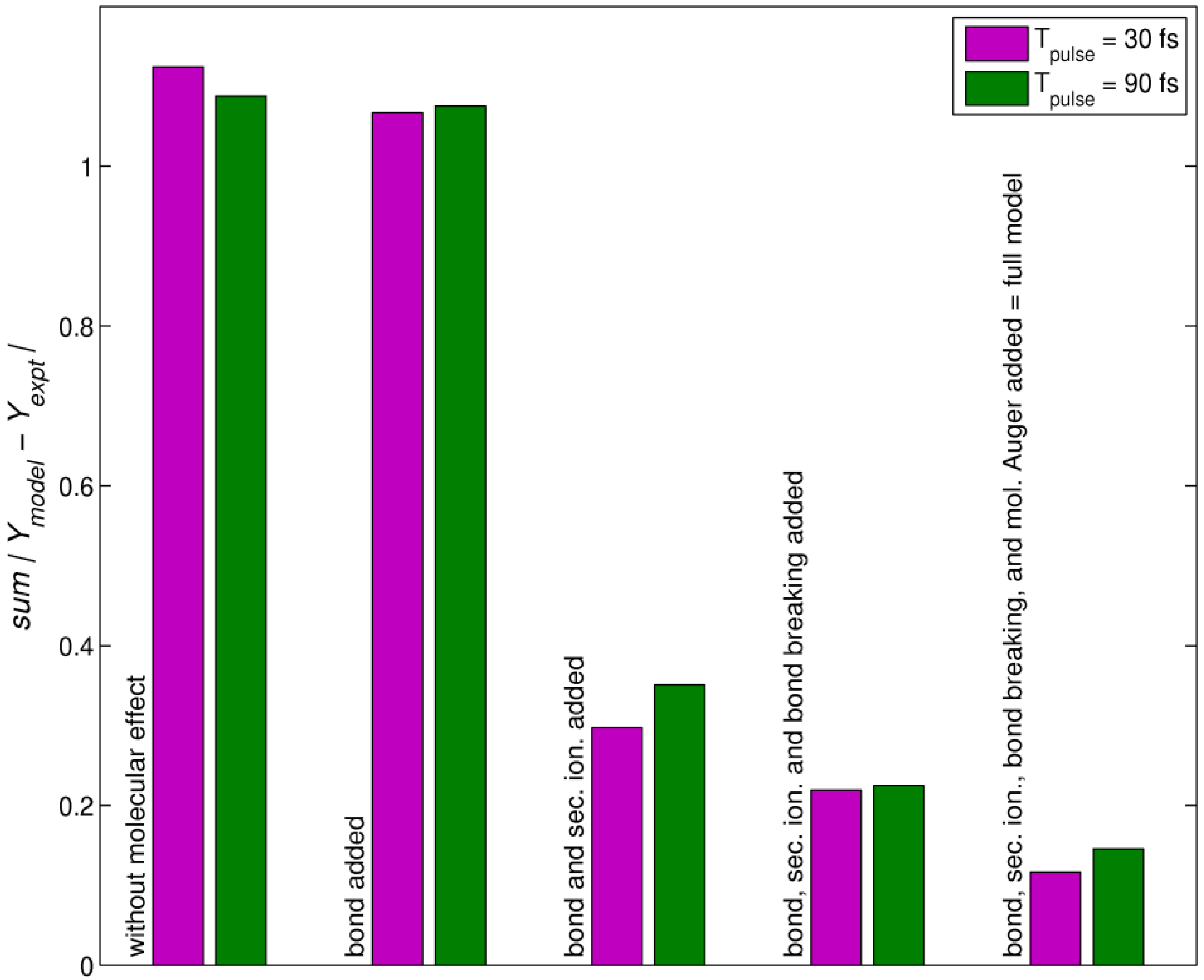
Time-Resolved Predictions: Coulomb explosion/expansion process; Final KE are reached at very short timescale.

Average atomic C charge state stops increasing due to recombination; secondary effects



T=0fs, Peak Fluence

Comparison of Experimental data with Molecular Dynamic model



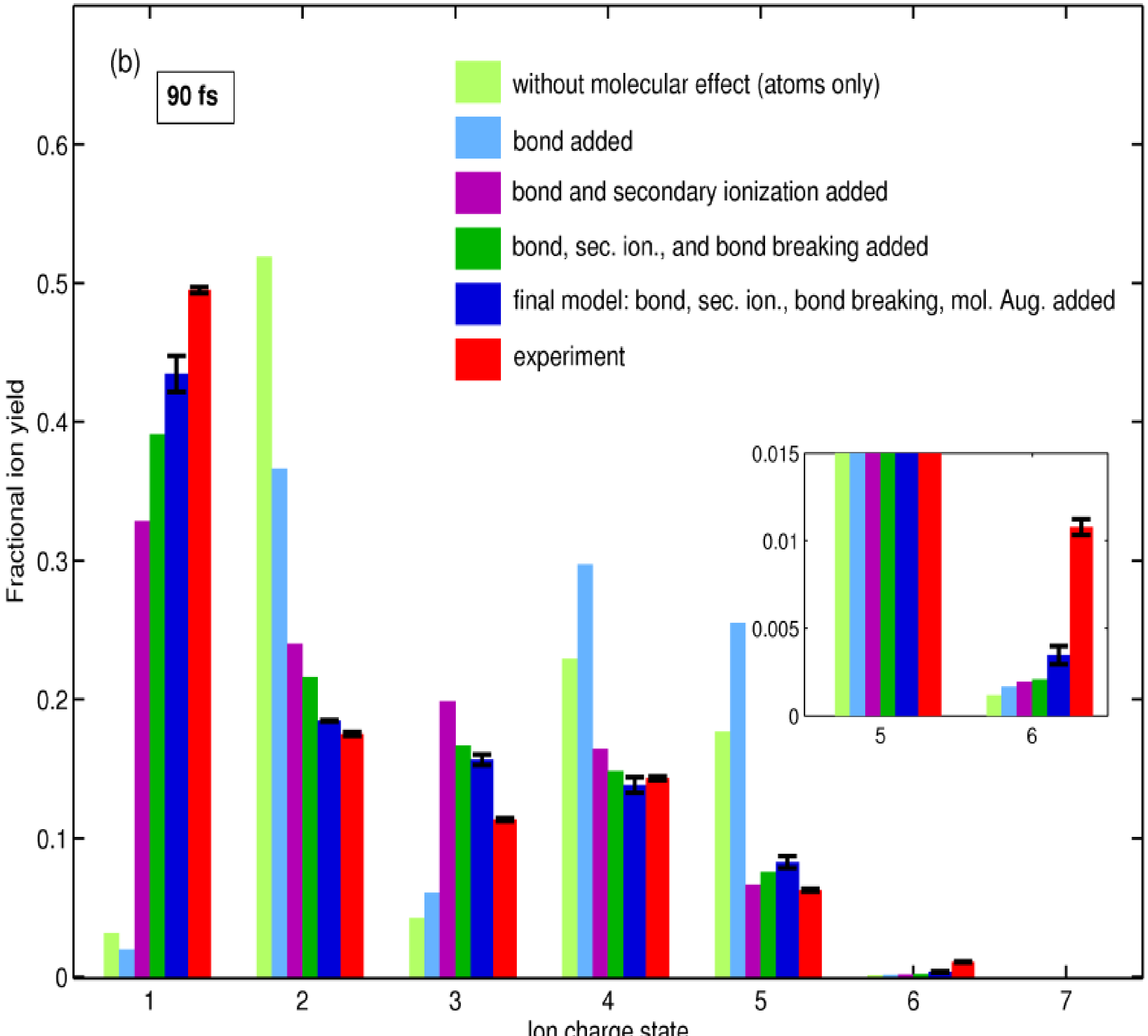
Validated a fundamental assumption: Charged particles behave as if they were classical particles

* **Significant secondary ionization by P and A e-** in C_{60} compared to Van der Waals clust.

* **Molecular influence are also strong** compared to VdW clust.

* C-C short bond length → **strong Coulomb repulsion**

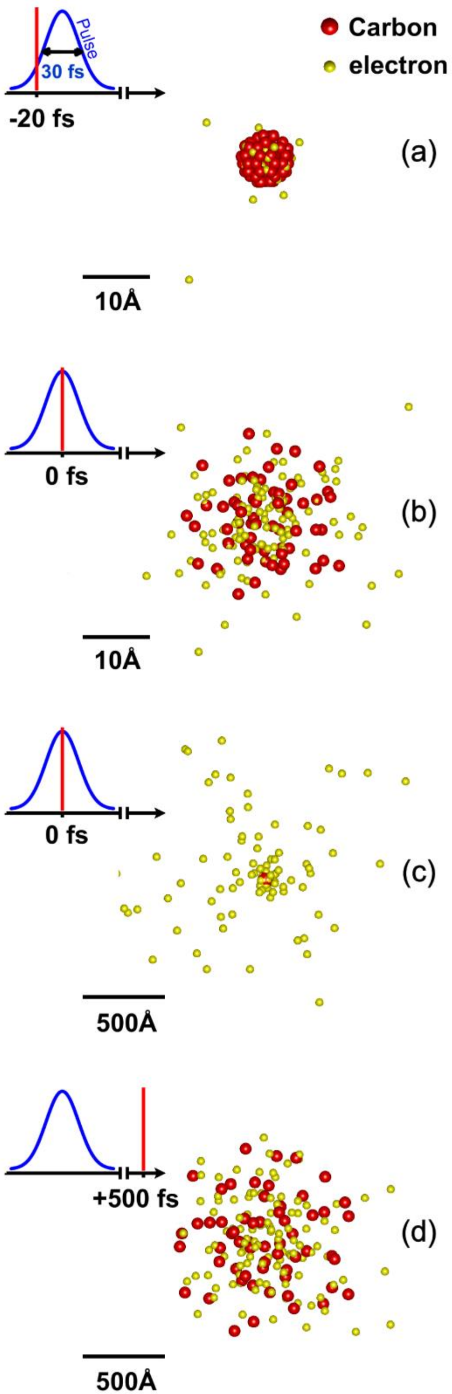
Comparison of Experimental data with Molecular Dynamic model



* **Significant** **secondary ionization by P and A e-** in C_{60} compared to Van der Waals clust.

* **Molecular influence are also strong** compared to VdW clust.

* C-C short bond length → **strong Coulomb repulsion**



Accepted proposal: Measure the time evolution of C_{60} molecules irradiated by XFEL pulses.

- **Highly charged C_{60} ions accumulate Coulomb potential energy.**
- **Ion repulsion leads to substantial atomic displacement (~10Å), and starts C_{60} explosion.**
- **Trapped electrons remain among the ions forming a nanoplasma.**
- **Within 100fs, recombination of e-&ions occurs leading to detected, suppressed ion charge states.**

Pulse duration is 30 fs, center of the pulse is at t=0 fs, pulse energy is 0.345 mJ. (Zoltan Jurek/Robin Santra)

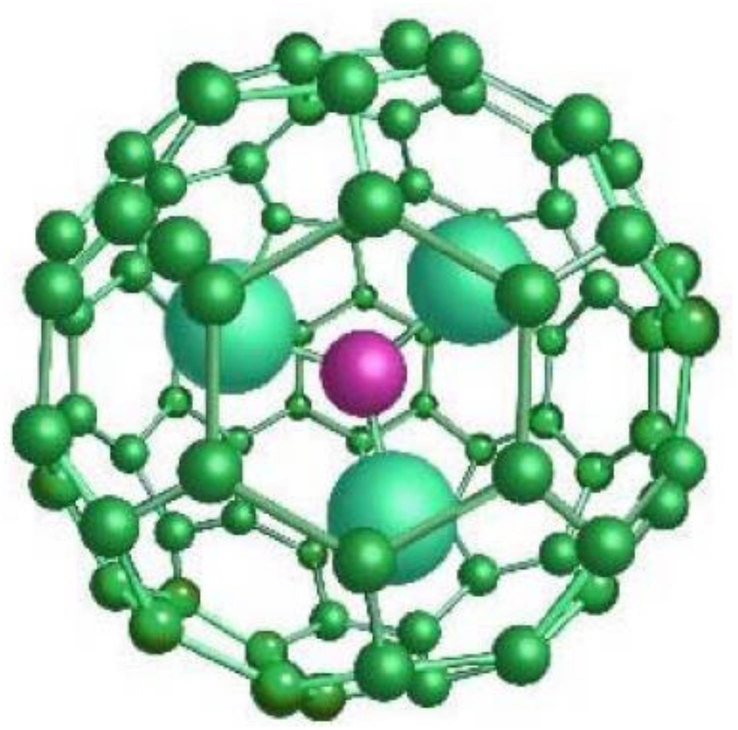
C^{0+}
C^{1+}
C^{2+}
C^{3+}
C^{4+}
C^{5+}
C^{6+}
e^{-}
-40.0fs

Next Goal: Time-Resolved Dynamics of Endohedral Fullerenes under Intense Exposure??

- High Z Endohedral Metalo-Fullerenes; Biological Diagnostic Tool; Possible safe contrast agent in imaging, MRI, for metastatic cancer;.

- Used in the Development of New Fullerene-based Drugs, therapeutic: Targeting and treating diseases.

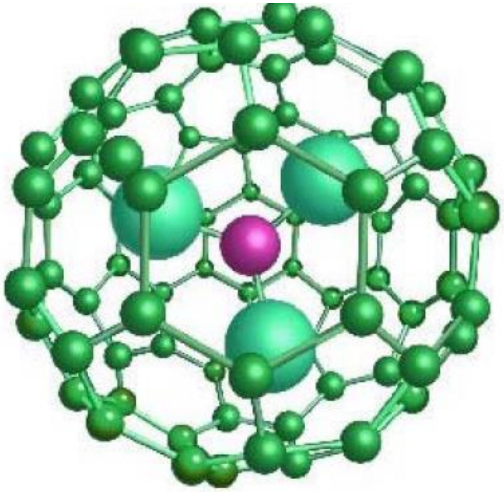
- These systems hold a potential in the advancement of Materials Design.



Model system

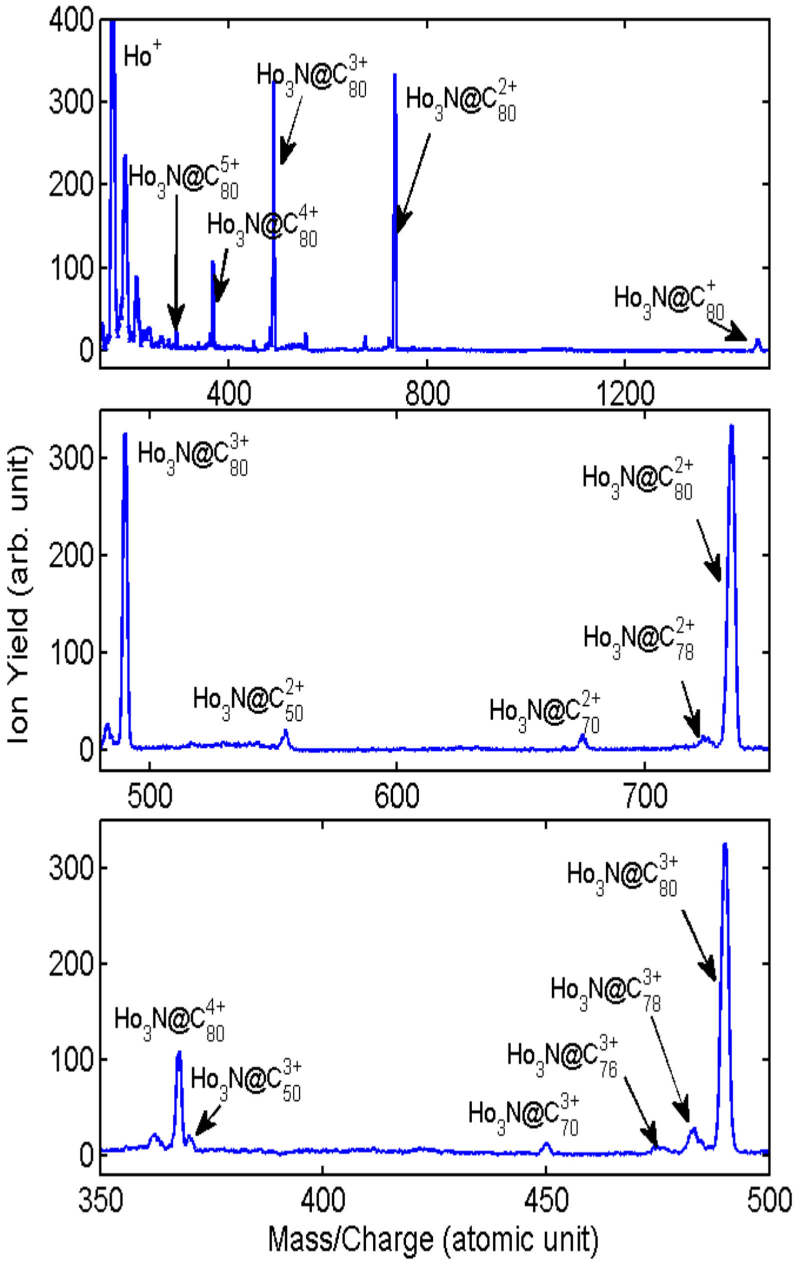
Goal: Ultrafast Electron and Nuclear Dynamics of Endohedral $Ho_3N@C_{80}$ Fullerenes with FELs

- Electron Transfer Dynamics from $Ho_3N \leftrightarrow C_{80}$

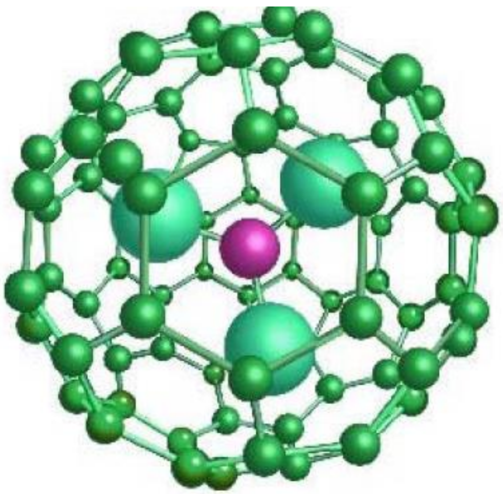


- Dynamics of Radiation Damage
  due to Auger cascades on carbon-bonded systems neighboring inorganic high-Z atoms.

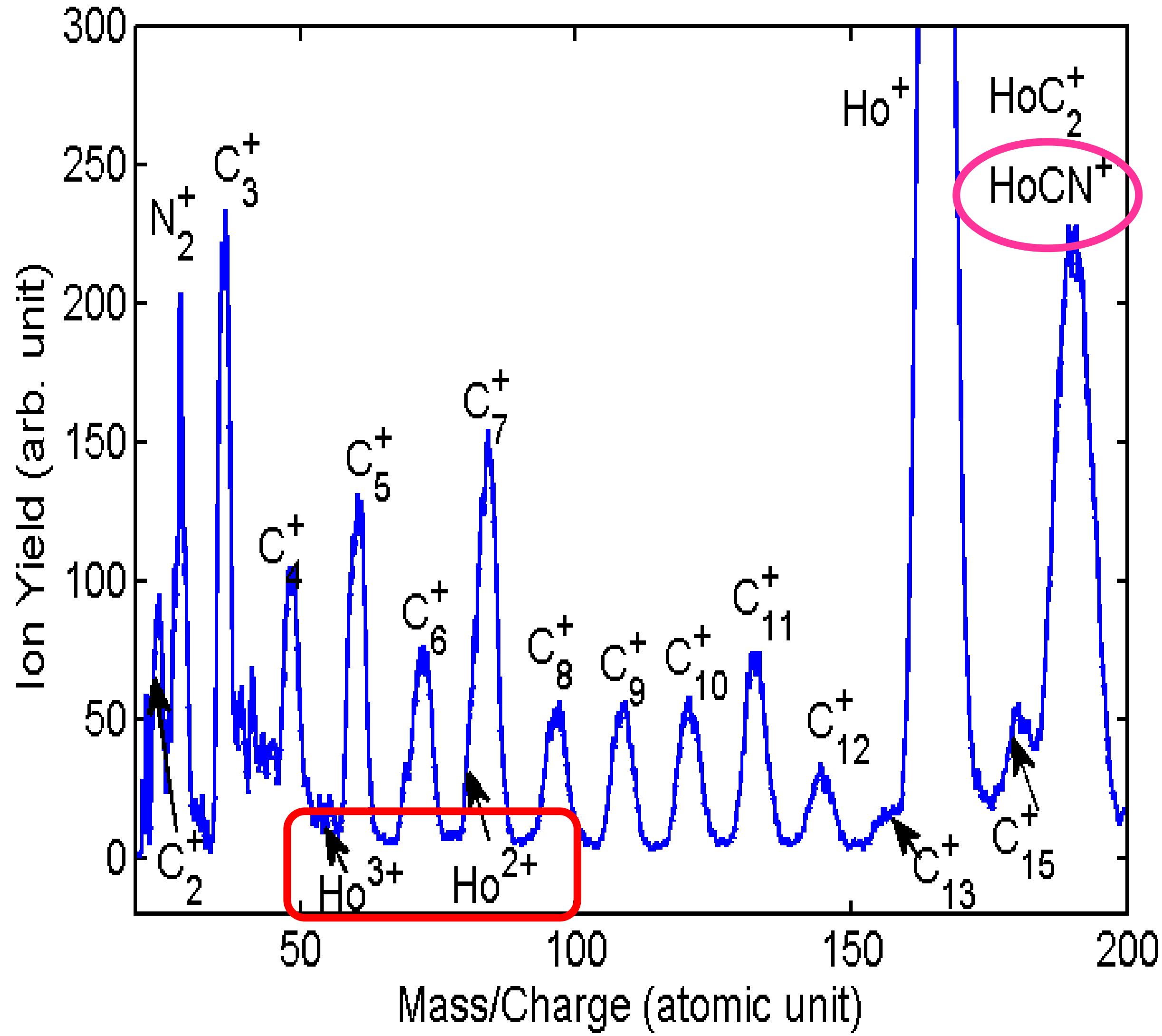
- Use pump-probe technique, 10 fs pulses of 1400–1500 eV photon energy, to track the evolution of ionization and fragmentation of $Ho_3N@C_{80}$.
  (high-Z (67) atoms dominate the x-ray photoabsorption).



Multiphoton X-Ray Induced Fragmentation of $Ho_3N@C_{80}$ at LCLS



Selectively target Ho 3d ionization hv=1530 eV, 80 fs, 2.2 mJ ~ 6.7 10^{18} ph/cm^2



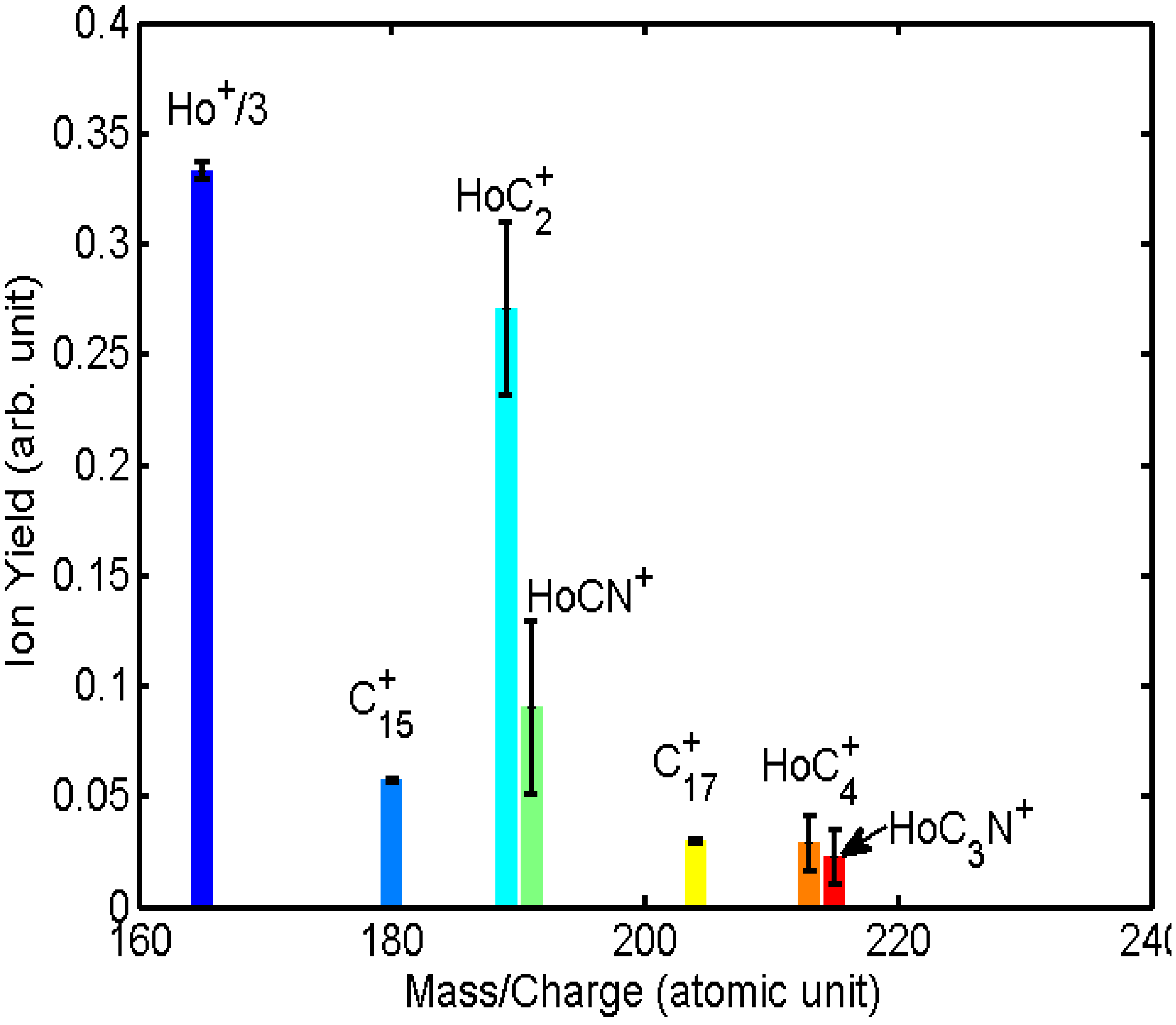
Ion yield displaying:

*Carbon molecular ion fragments **(medium Fluence)**

***Ho charge states**

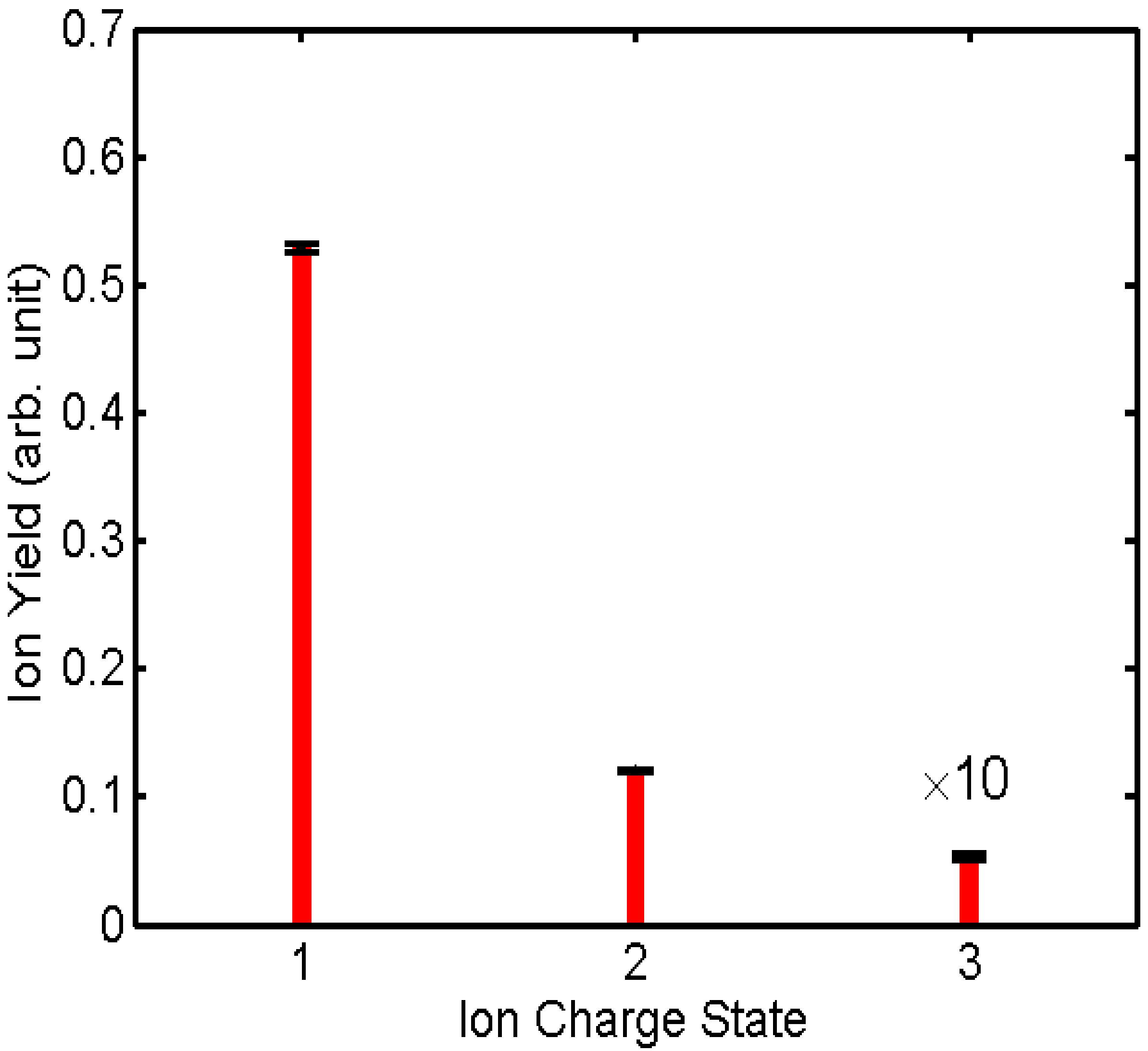
* **Bond forming**

Ion Yield Fragments: Ho^+ and Ho-based molecular ion fragments



Bond forming: HoC_2^+, $HoCN^+$, HoC_4^+, HoC_3N^+

Carbon ion yield for the charge states of C^{+} - C^{3+}



σ_{C80}=1Mb
(σ_{C}= 0.013 Mb)

σ_{3Ho}=3.9 Mb
($\sigma_{Ho\text{-}3d}$= 1. 3 Mb)

@1530 eV

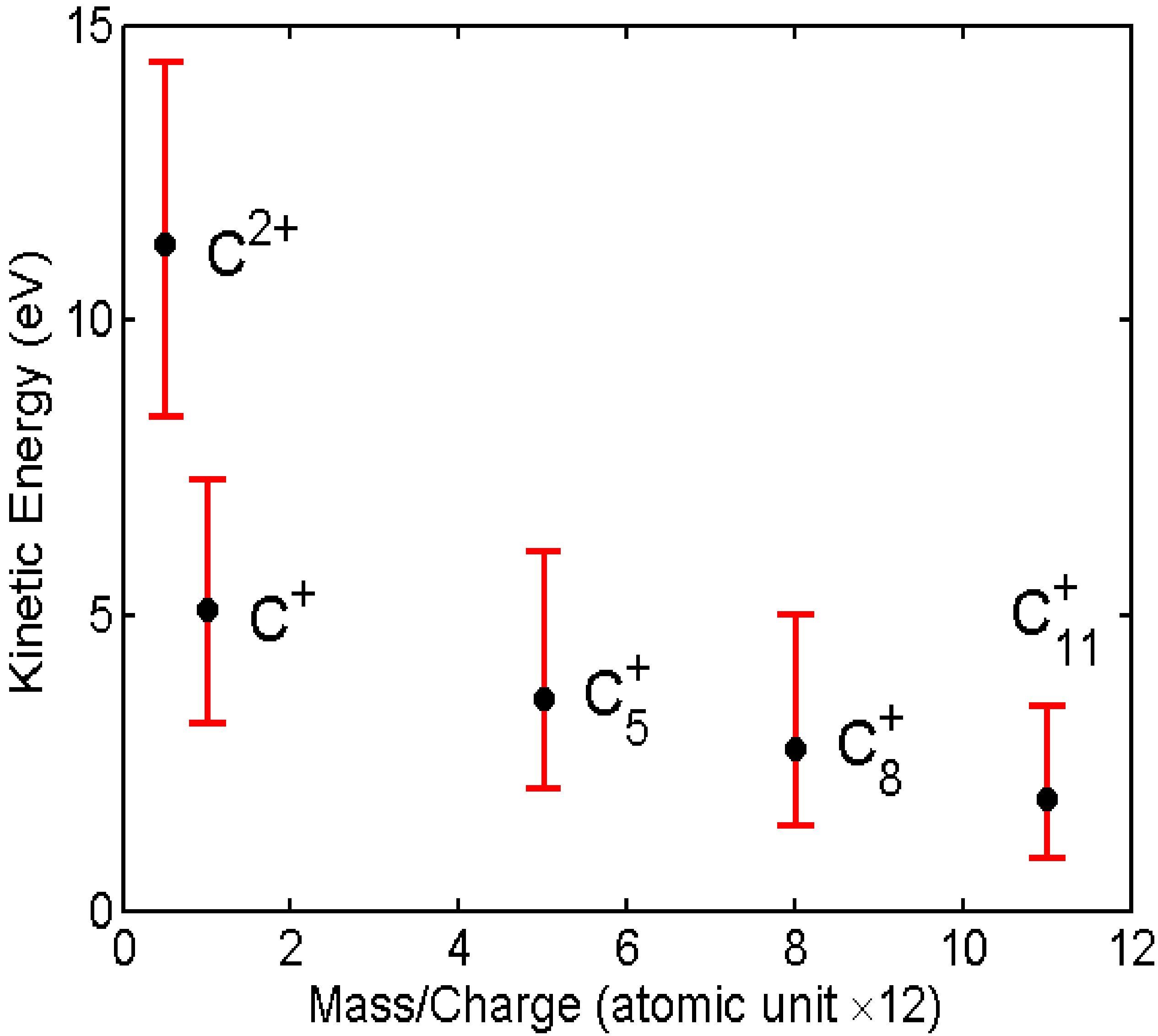
Normalized branching ratios of selected ion fragments.

Ion	Ho^+	Ho^{2+}	$Ho_3N@C_{80}^+$	$Ho_3N@C_{80}^{2+}$	$Ho_3N@C_{80}^{3+}$	$Ho_3N@C_{80}^{4+}$	$Ho_3N@C_{80}^{5+}$
Yield (%)	100	4.8	0.83	12	8.3	2.3	0.47
Ion	C^+	C^{2+}	C^{3+}	HoC_2^+	$HoCN^+$	HoC_4^+	HoC_3N^+
Yield (%)	53	12	0.53	27	9.0	2.9	2.3

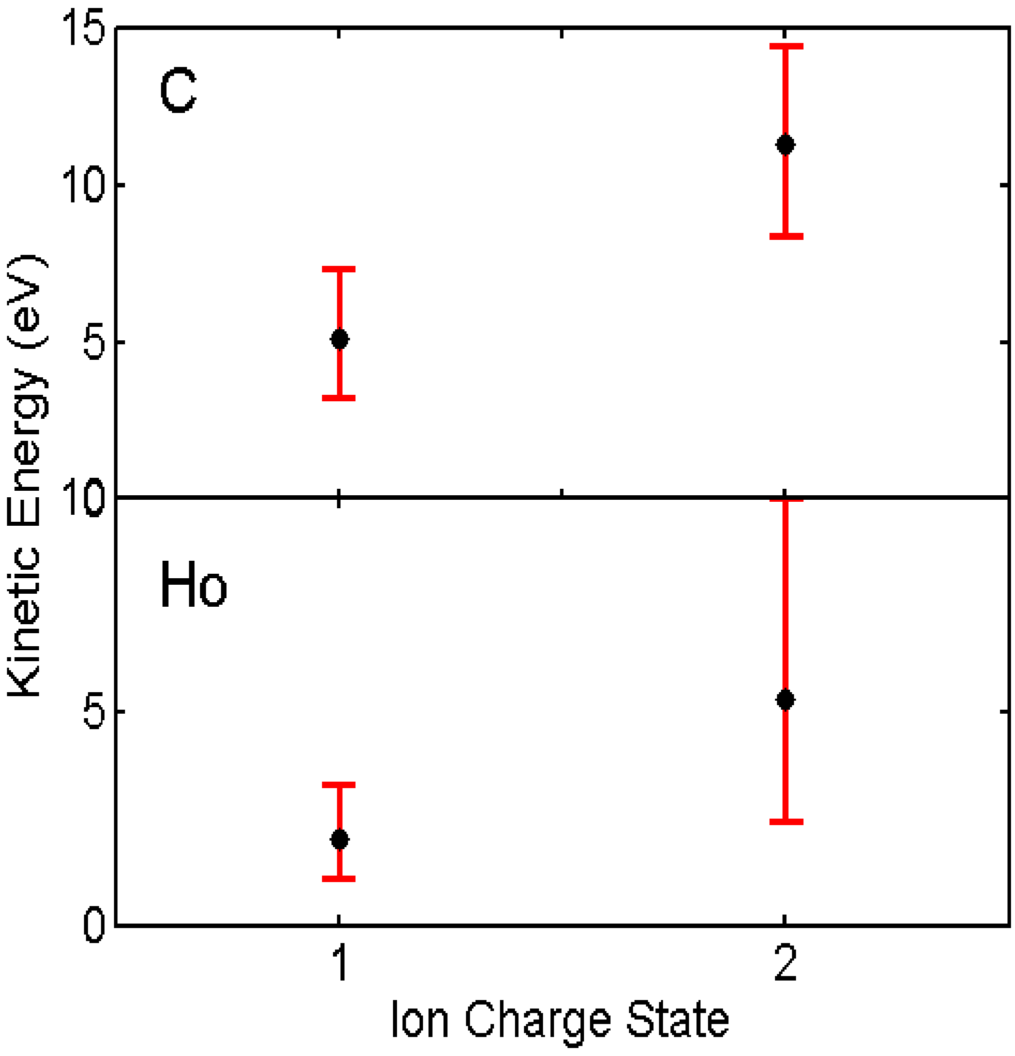
σ_{C80} =1Mb

$\sigma_{3Ho\text{-}3d}$= 3.9 Mb

Kinetic energy for selected atomic and molecular C fragments



Kinetic energy for atomic C and Ho ion fragments

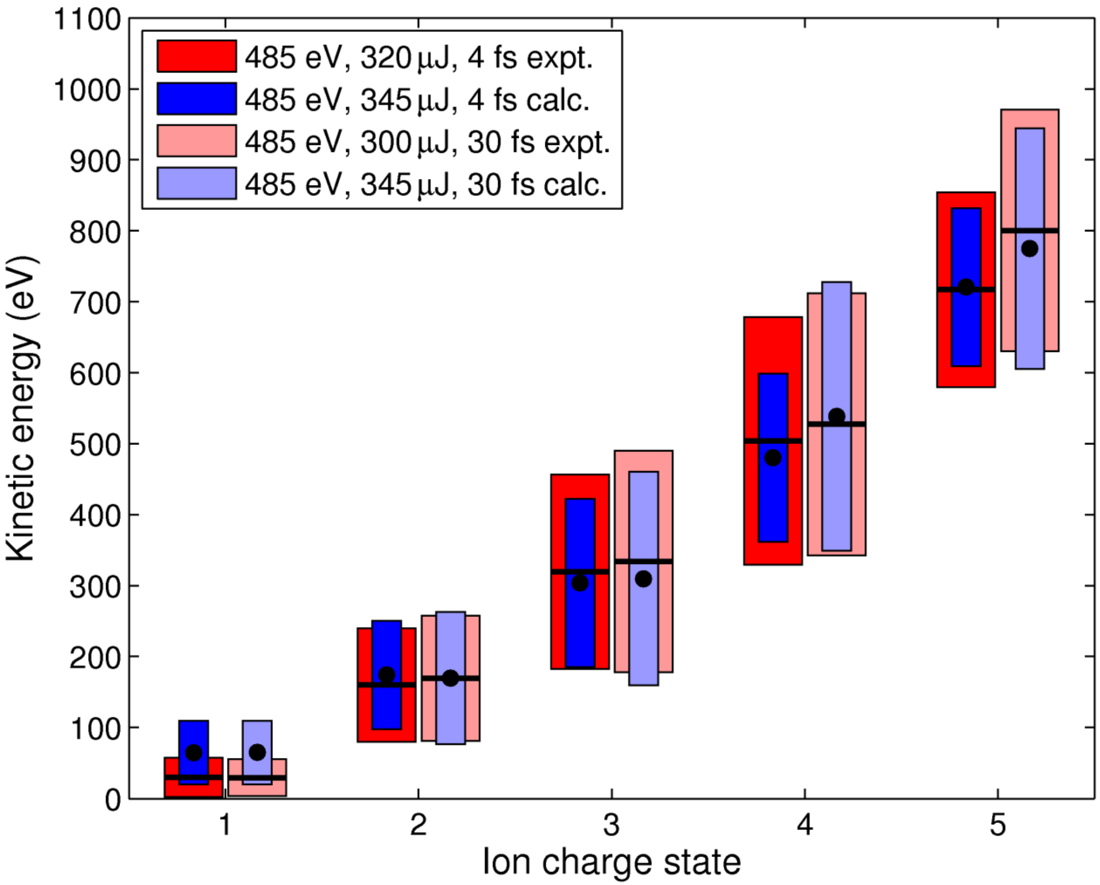


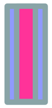
σ_{C80}=1Mb

σ_{3Ho}=3.9 Mb

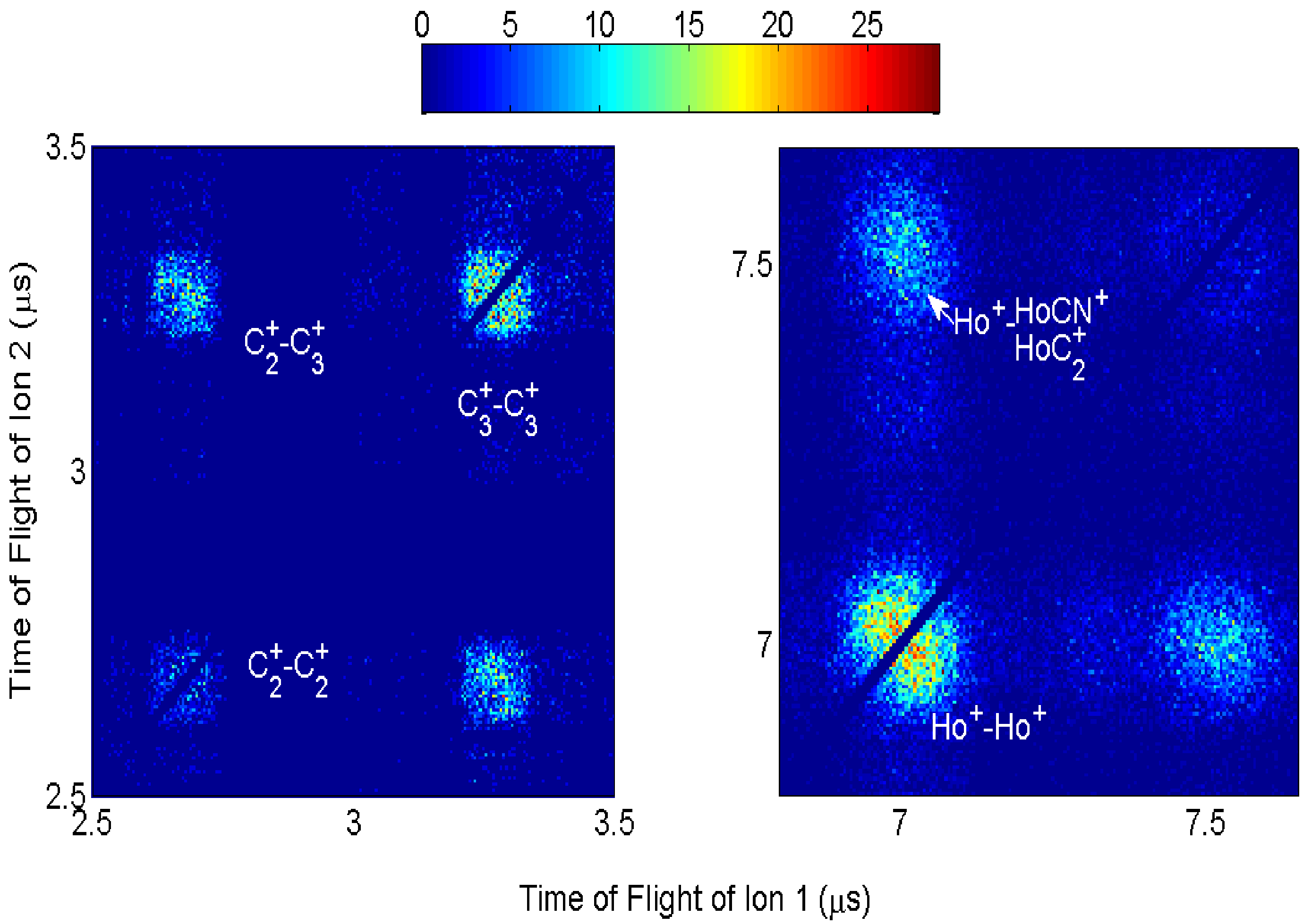
@1530 eV

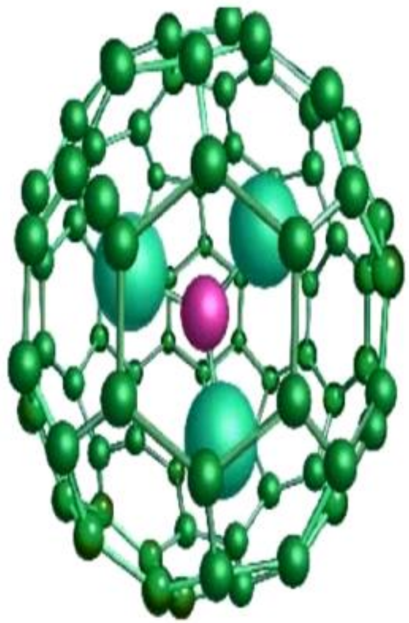
Nanoplasma characterization: Fragment Atomic C Ion Kinetic Energy (Central high-fluence region)



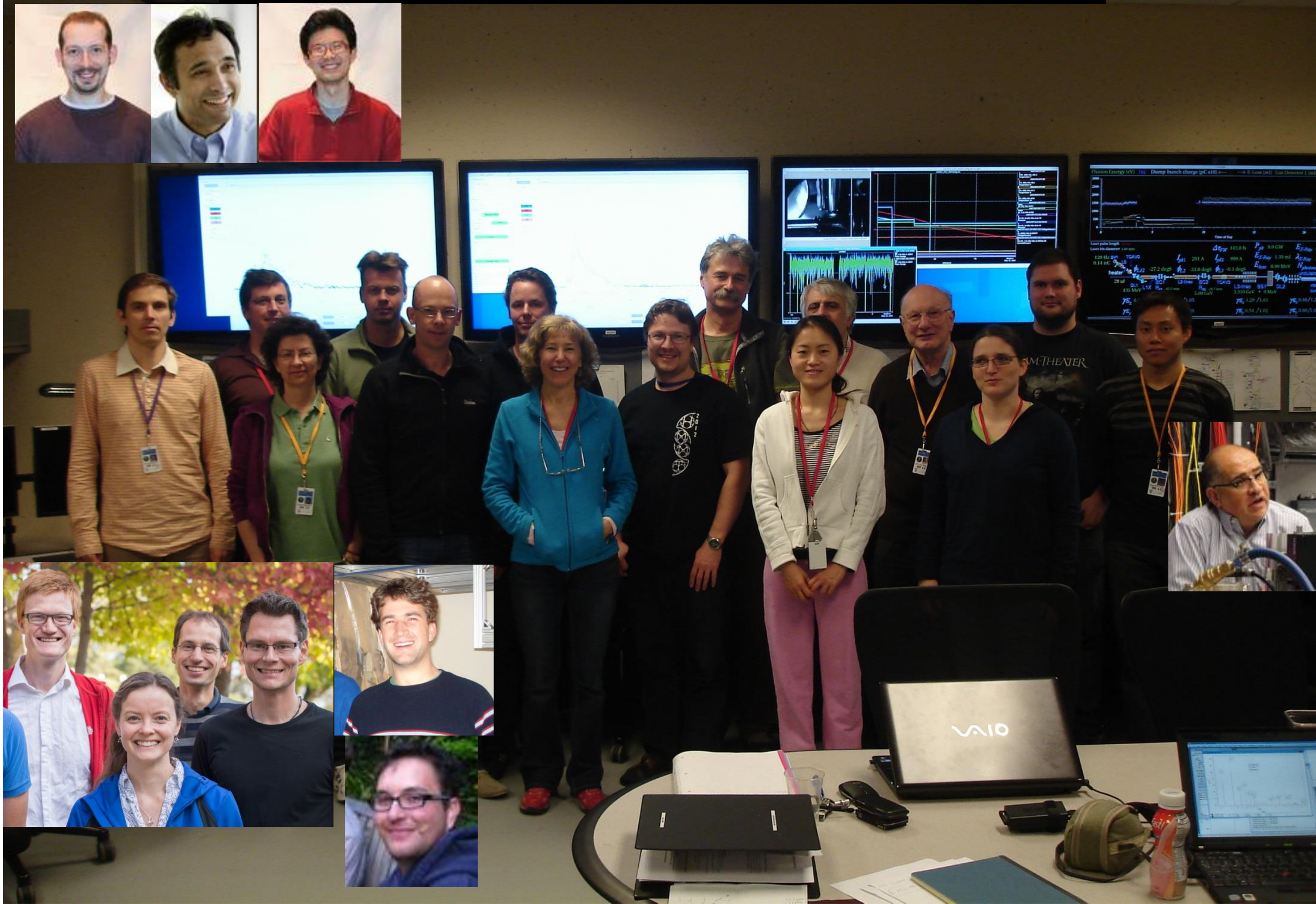
Mean ion kinetic energy: **circles** **(experiment)** and **lines** **(simulation).**
RMS kinetic energy width: Height of each rectangle. 

Covariance map of small molecular fragments





C_{60} Collaboration Experiment



$Ho_3N@C_{80}$ Collaboration

B. Murphy, H. Xiong, L. Fang, T. Osipov, E. Kukk, M. Guehr, R. Feifel, V. S. Petrovic, K. R. Ferguson, J. D. Bozek, C. Bostedt, L. J. Frasinski, P. H. Bucksbaum, J. C. Castagna, N.Berrah

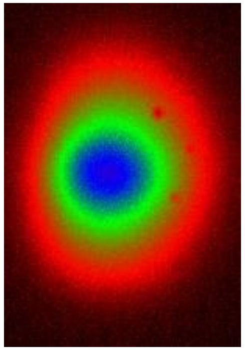
Need Advanced Tools and Methods for New Science!

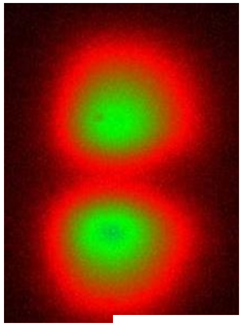
LAMP: New Multi-User Instruments Capabilty @ LCLS afforded by DOE-Sc SISGR Grant: AMO, CHEM, Solid State/Material Science, Plasma, MEC, BIO…

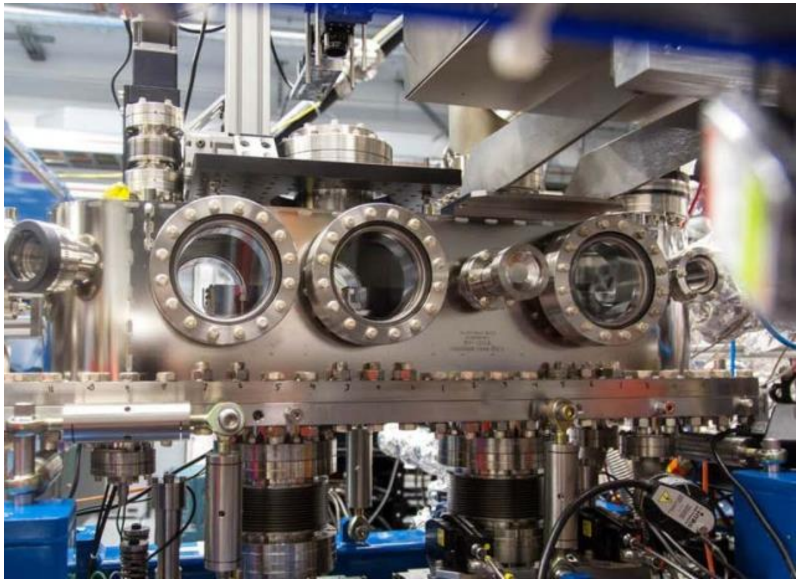
- ✓ **Time-Resolved Spectroscopy/Dynamics: to track the motion of nuclei in molecules/nano-systems.**

- ✓ **Imaging: Diffraction Imaging techniques to freeze in time the motion of complex molecules/extended systems**

Time-Resolved Dynamics: *Soft X-Ray Split and Delay (XRSD) System for* Femtosecond X-Ray Pump X-Ray Probe Science at LCLS (May 2013)







Features of XRSD

- ✓ 'Jitter free' pump-probe
- ✓ Identical temporal profiles

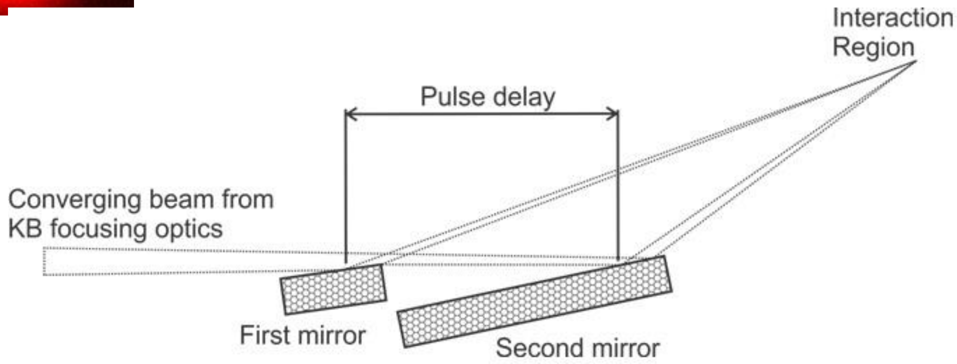
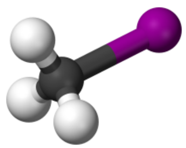


Image of the pump (top) and probe (bottom) pulses from the XRSD separated by 150 fs on the laser cross-correlation time-tool paddle *(time increases to the right).*

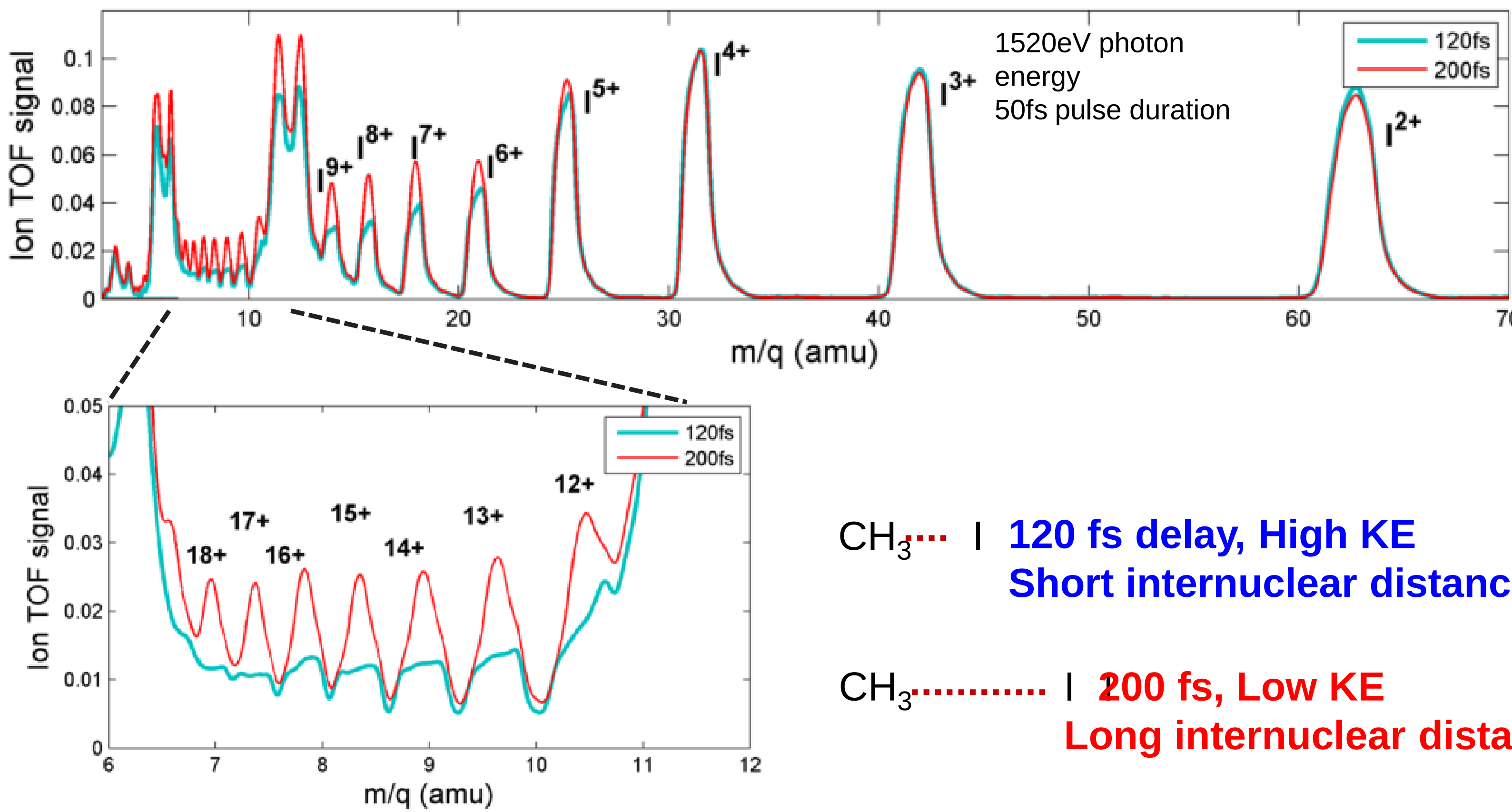
UCONN UNIVERSITY OF CONNECTICUT · LCLS

Pump-probe - Methyl Iodine commissioning



CH_3I

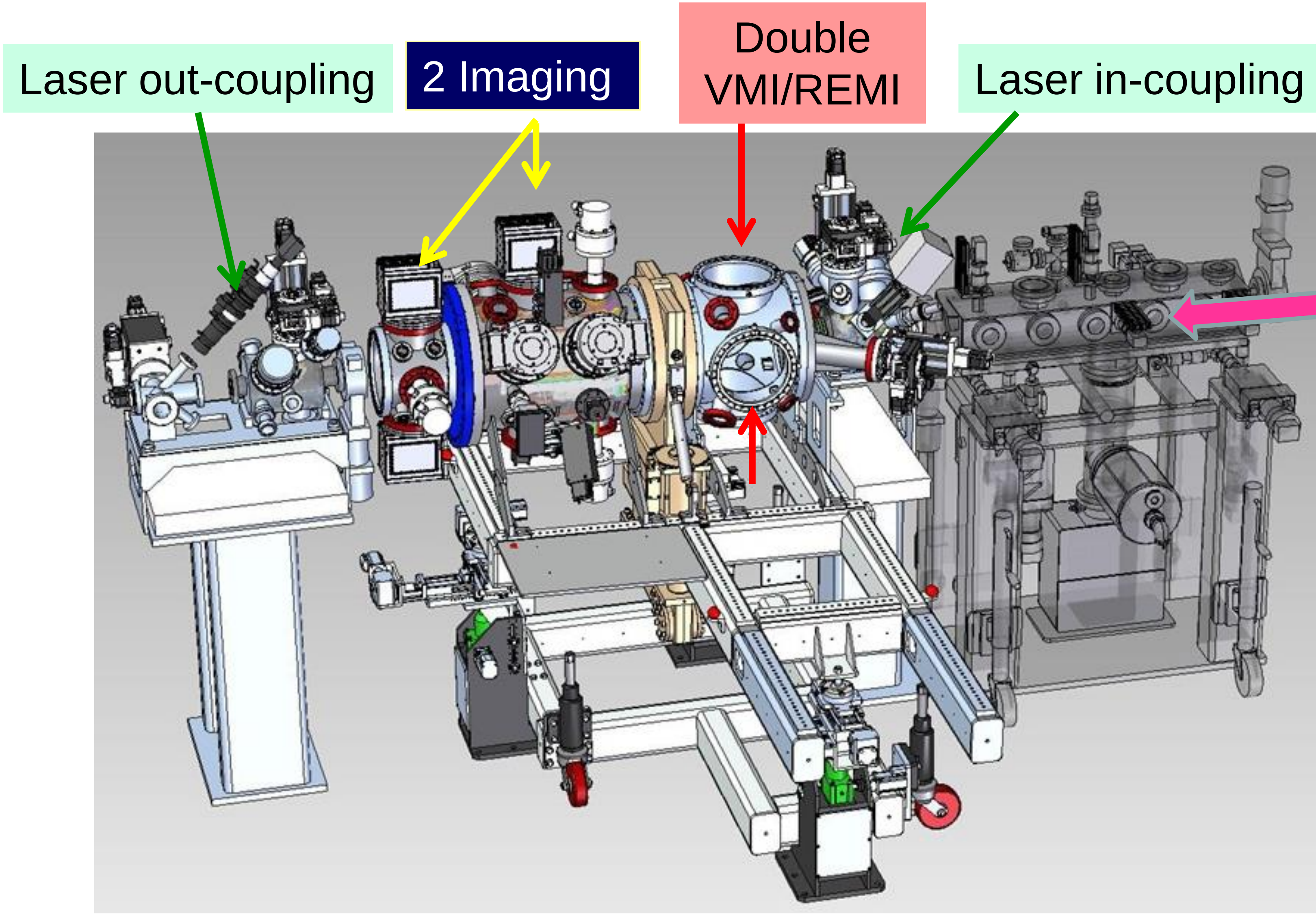
Different pump-probe delays



CH_3···· I **120 fs delay, High KE**
Short internuclear distance

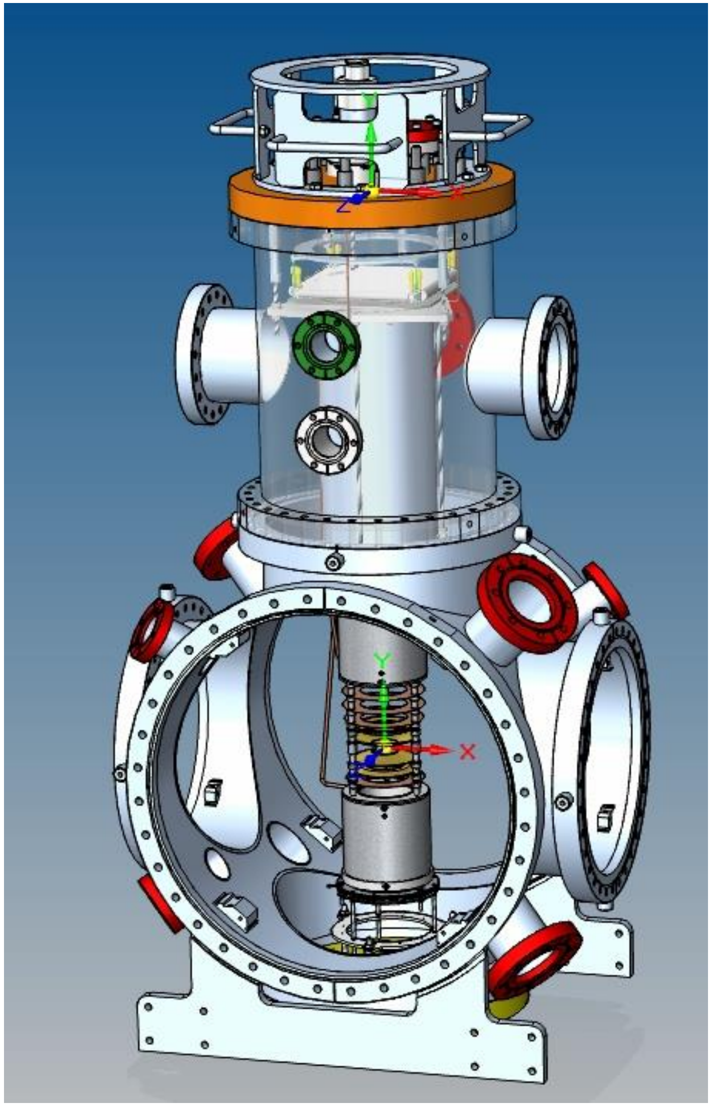
CH_3············ I **200 fs, Low KE**
Long internuclear distance

Additional Capability: LAMP Multi-Purpose Instruments (Nov 2013)

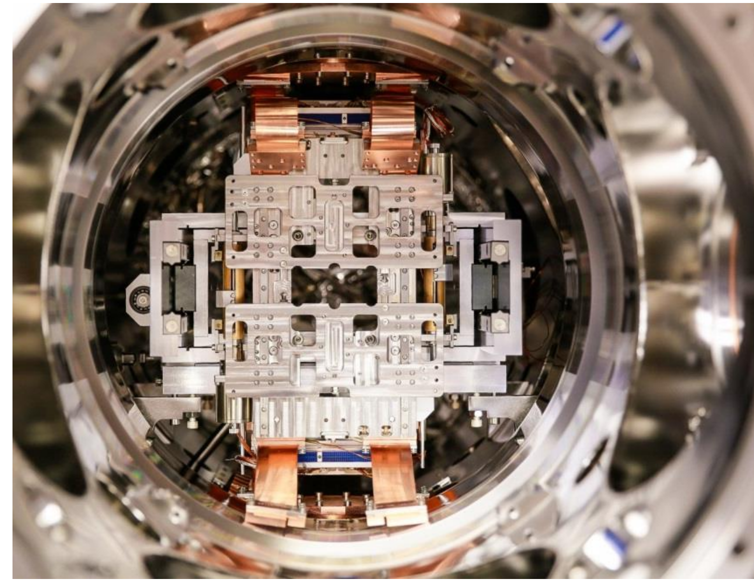


Model-CAMP, Struder , Epp, Rolles, Rudenko, Ullrich… NIM A **614**, 483,’10

Double VMI/REMI



Large Area X-ray pnCCD Detector



MPI Semiconductor Lab (Munich):

1024x1024 pixels

pixel size: 75 x 75 μm^2

active area: 59 cm^2

frame rate: up to 200 Hz

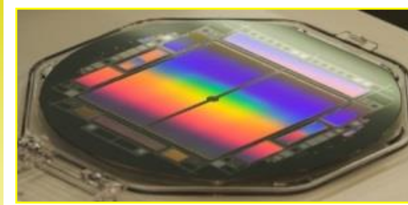
single-photon resolution

up to 10^3 photons (1keV) per pixel

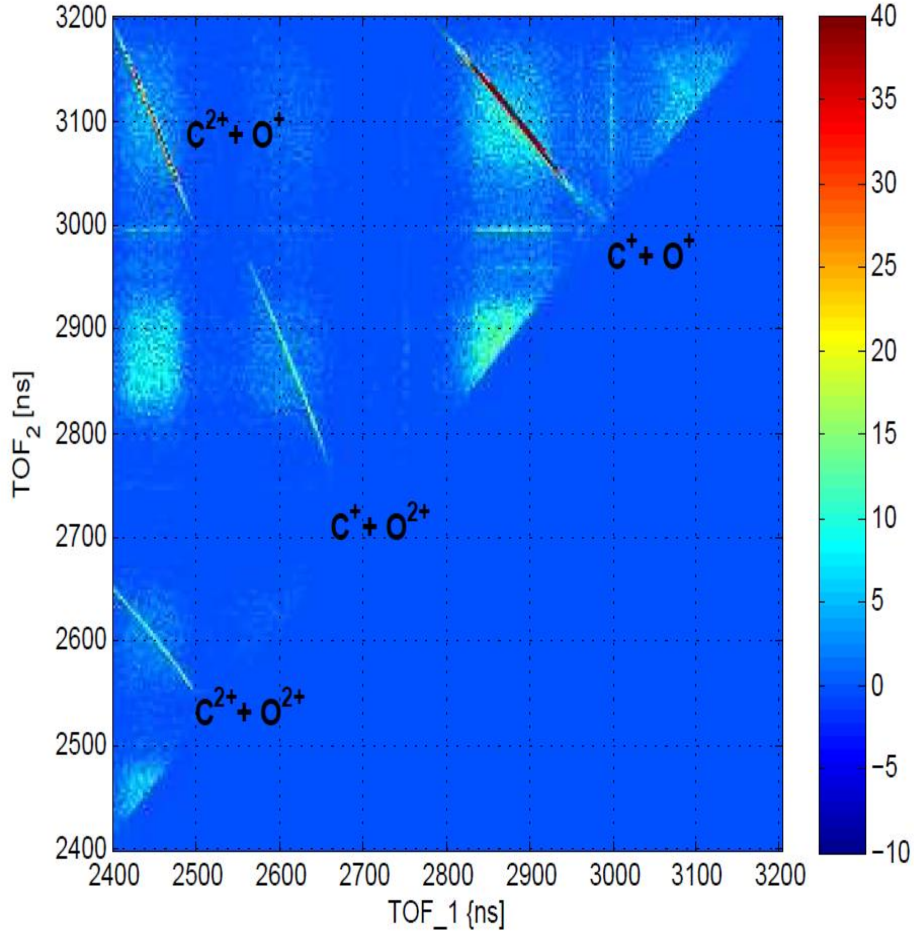
$\Delta E/E \sim 5\%$ (800eV to 2000eV)

Q.E. $\geq$ 90 % from 0.8 to 10 keV

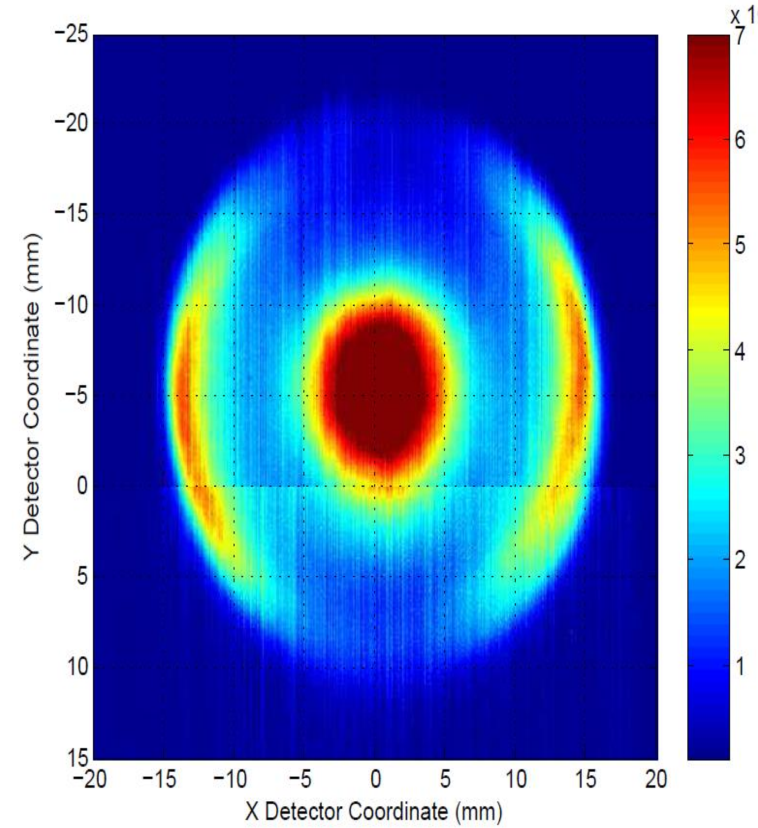
operating range $0.1 < E < 25$ keV



UCONN UNIVERSITY OF CONNECTICUT LCLS



Ion-Ion Coincidence Events recorded during ionization of CO with 430 eV X-rays with 5fs pulse duration.



Electron spectra recorded for ionization of Ne. Outer ring: Ne 1s photoelectron diplole angular distribution.

XRSD & LAMP: Team Effort

University of Connecticut & LCLS/SLAC

Planning, Design, Assembly, Controls, Alignment

J.-C.Castagna, T. Osipov, B. Murphy, M. Swiggers, M. Bucher, D. Stefanescu, P. Noonan, I. Curiel, S. Carron-Montero, E. Rodriguez, J. Whitaker, D. Cocco, T.Catalano, N. Kelez, M. Rogers, M. Gaydosh, G. Gassner, J. Bozek, C. Bostedt and N. Berrah.

Commissioning

Those above, plus K.Ferguson, E. Kukk, A. Rudenko, D. Rolles, L. Fang, H. Xiong, G. Dakovski, J. Krzywinski, R. Coffee,P. Bucksbaum, J.Devin, V. Petrovic, B. Schlotter, J. Turner.

UCONN
UNIVERSITY OF CONNECTICUT

DEPARTMENT OF ENERGY · UNITED STATES OF AMERICA

LCLS

Next Instrument: Fluorescence Spectrometer

(in preparation)

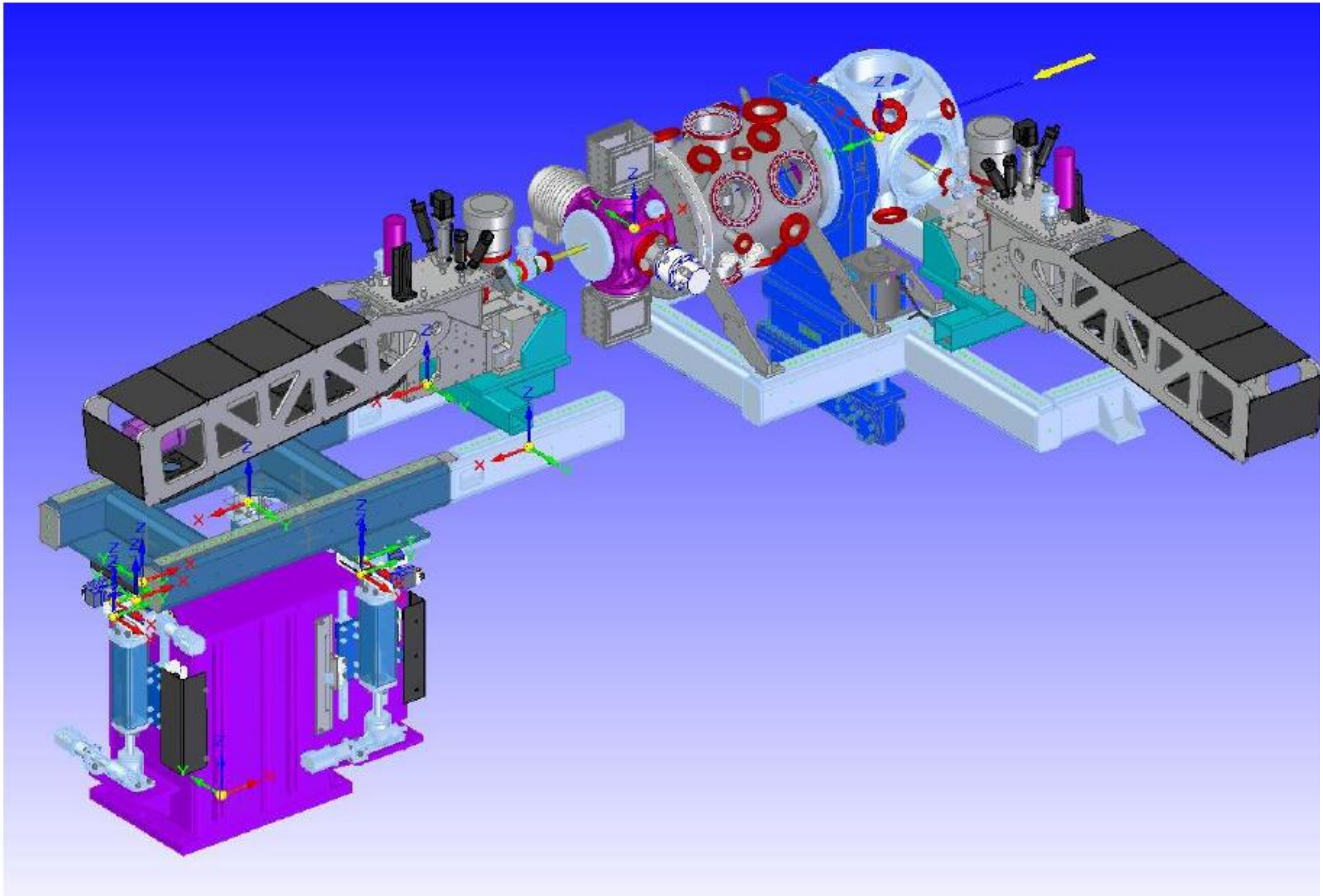
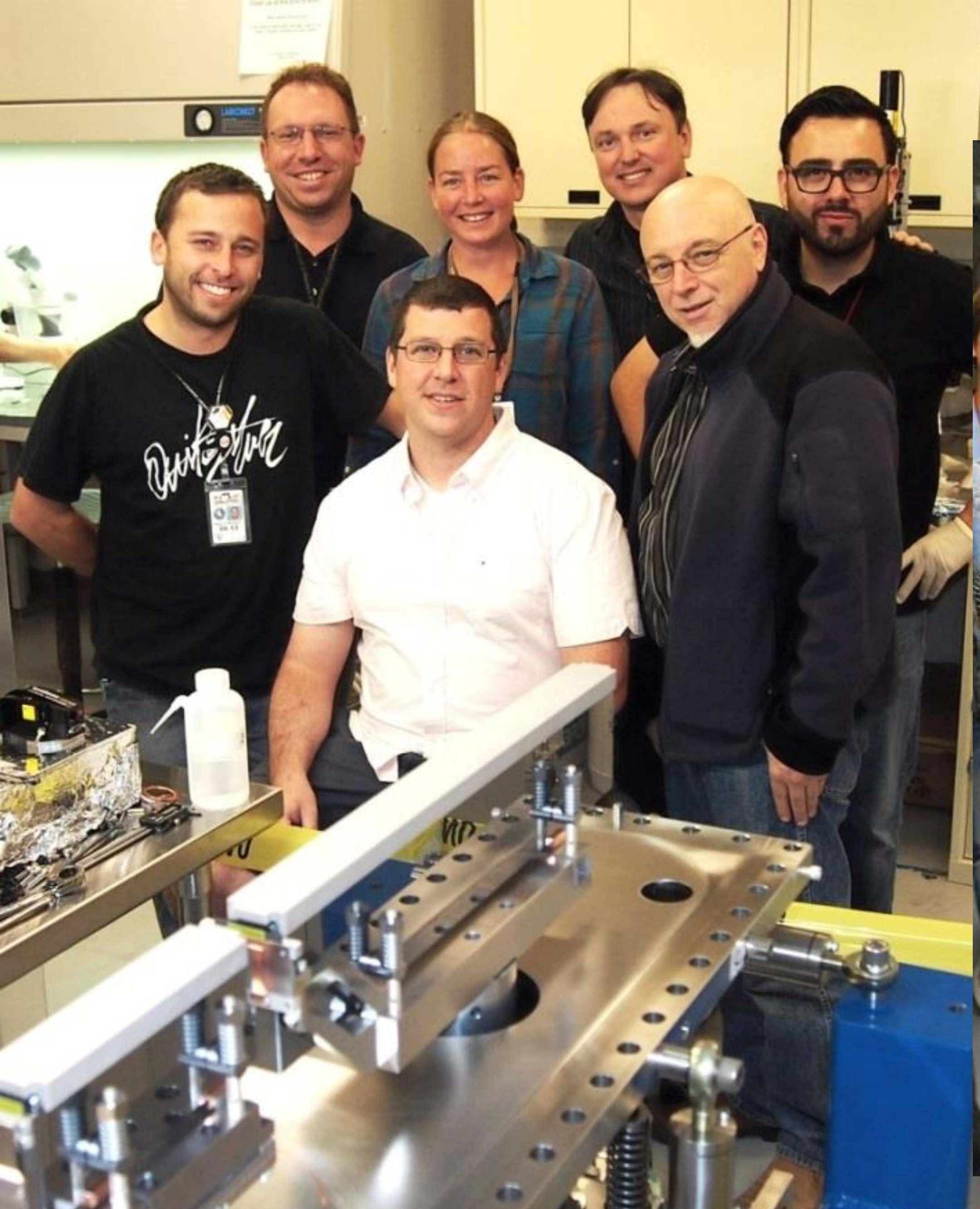
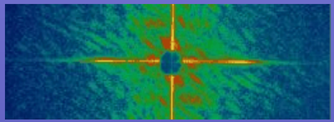


Figure 1: CAD model of the spectrometer installed on the AMO LAMP instrument. Two configurations, forward and 90º horizontal are shown.





- *FLASH* at *DESY* (4 - 45 nm) 2005
- *LCLS* at *SLAC* (0.12 - 2.5 nm) 2009
- *Fermi* in *Trieste, Italy* (4 - 80 nm) 2010
- *SACLA* at *SPring-8*, Japan (0.1-3.6 nm) 2011
- *European X-FEL* at *DESY* (0.1 - 6 nm) **2017**
- *Swiss-FEL* at *PSI* (0.1 - 7 nm) **2017**
- *PAL-XFEL* in *Korea* (0.1 - 10 nm) **2017**
- *LCLS-II* at *SLAC* (0.05 - 6.2 nm) **2019**

Photon Sources? Planned-Existing X-ray FELs

Future: Bright and Fun! Time Resolved Studies @ MUCH Shorter Pulses at LCLS with XRSD or TWO colors (optical or x-ray)

Seeded FEL beam

(narrower bandwidth approaching the transform limit)

✓ Demonstration of the hard X-ray Self-Seeding.

Nature Photonics (2012)

❑ Soft X-ray region is underway

(grating monochromator in Undul).

Few fs mode established:

- **Reducing electron bunch charge from 250pC to 20pC** (shorter electron bunch).

1 fs pulses is possible

Y. Ding, PRL **102**, 254801(2009)

Atto mode:

possible with ECHO technique

Co-propagation of laser and electron bunch in wiggler Results in micro-bunching (PRL **102**,(2009))

Collaboration ('10) DCH/TOFs