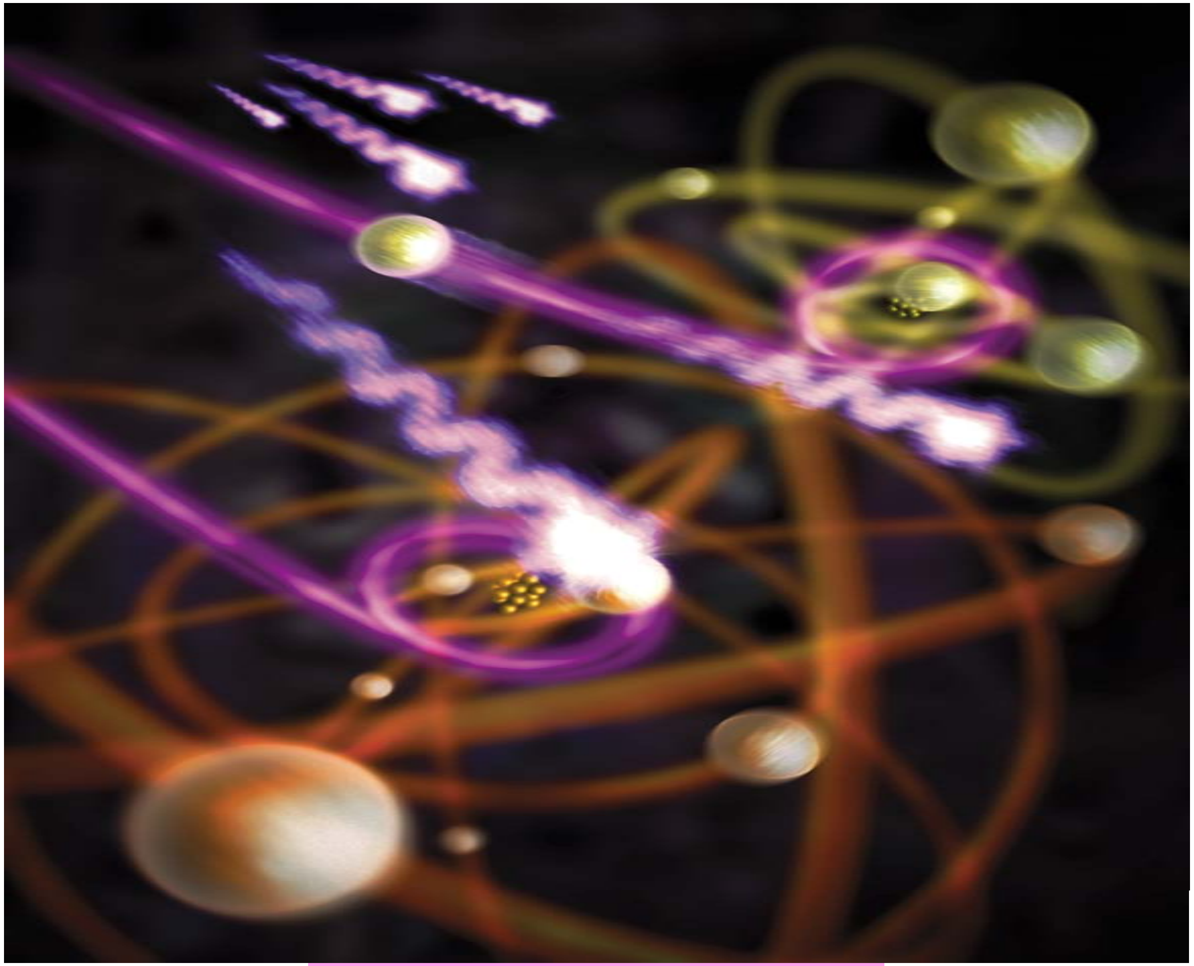
Probing Molecules from Within using LCLS

Nora Berrah,
Physics Dept, Western Michigan University



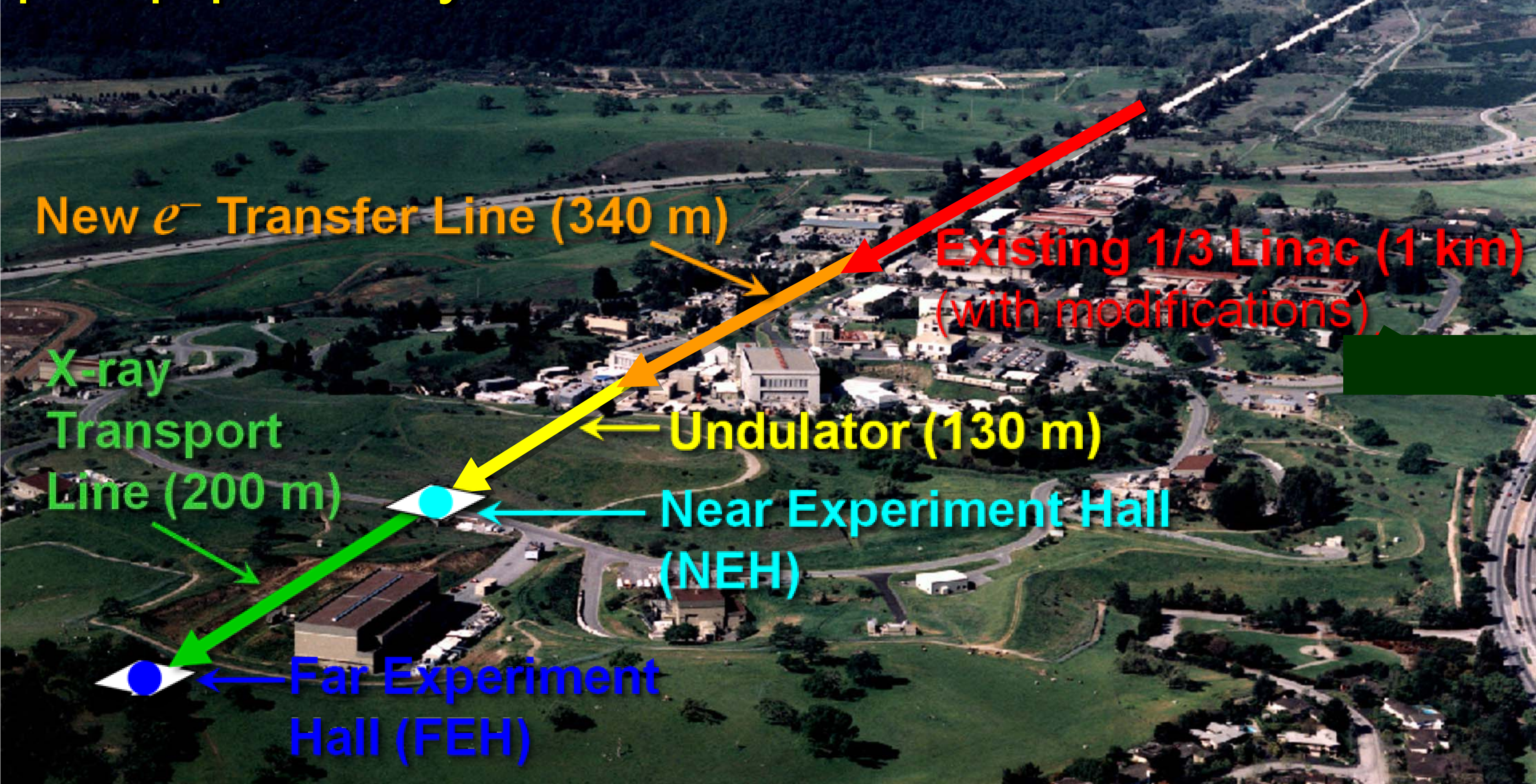
Funded by DOE-BES

Outline

- Introduction/Motivation
- Experimental Method
- Multiphoton Ionization & Frustrated Absorption in Molecules
- Double Core Hole Spectroscopy in Molecules
- Future work

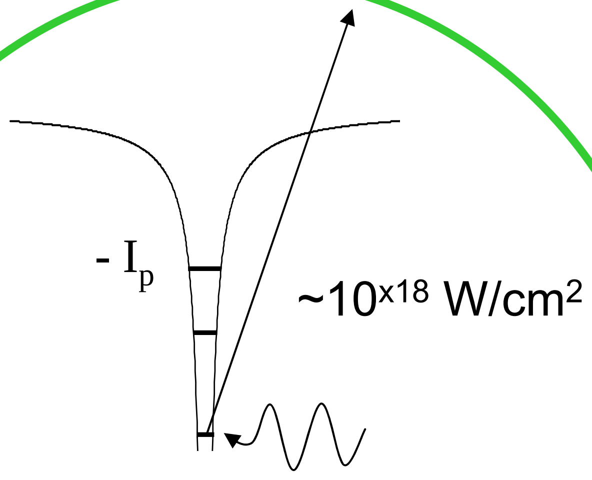
LCLS at SLAC: X-FEL based on last 1-km of existing 3-km linac; (15-3.3 GeV)

- **480 eV-10KeV; < 5 - 500 fs; up to 4 mJ; 120 fs** pump-probe synchronization



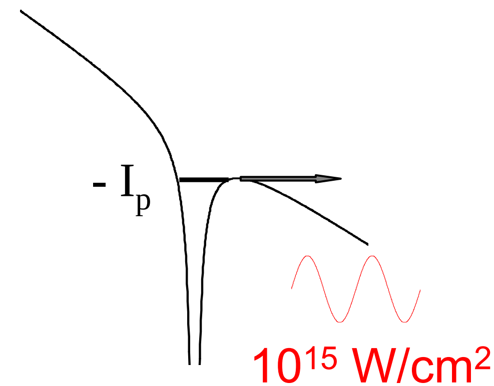
Ultraintense and Ultrafast X-FEL & IR Sources: Different Ionization Processes

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

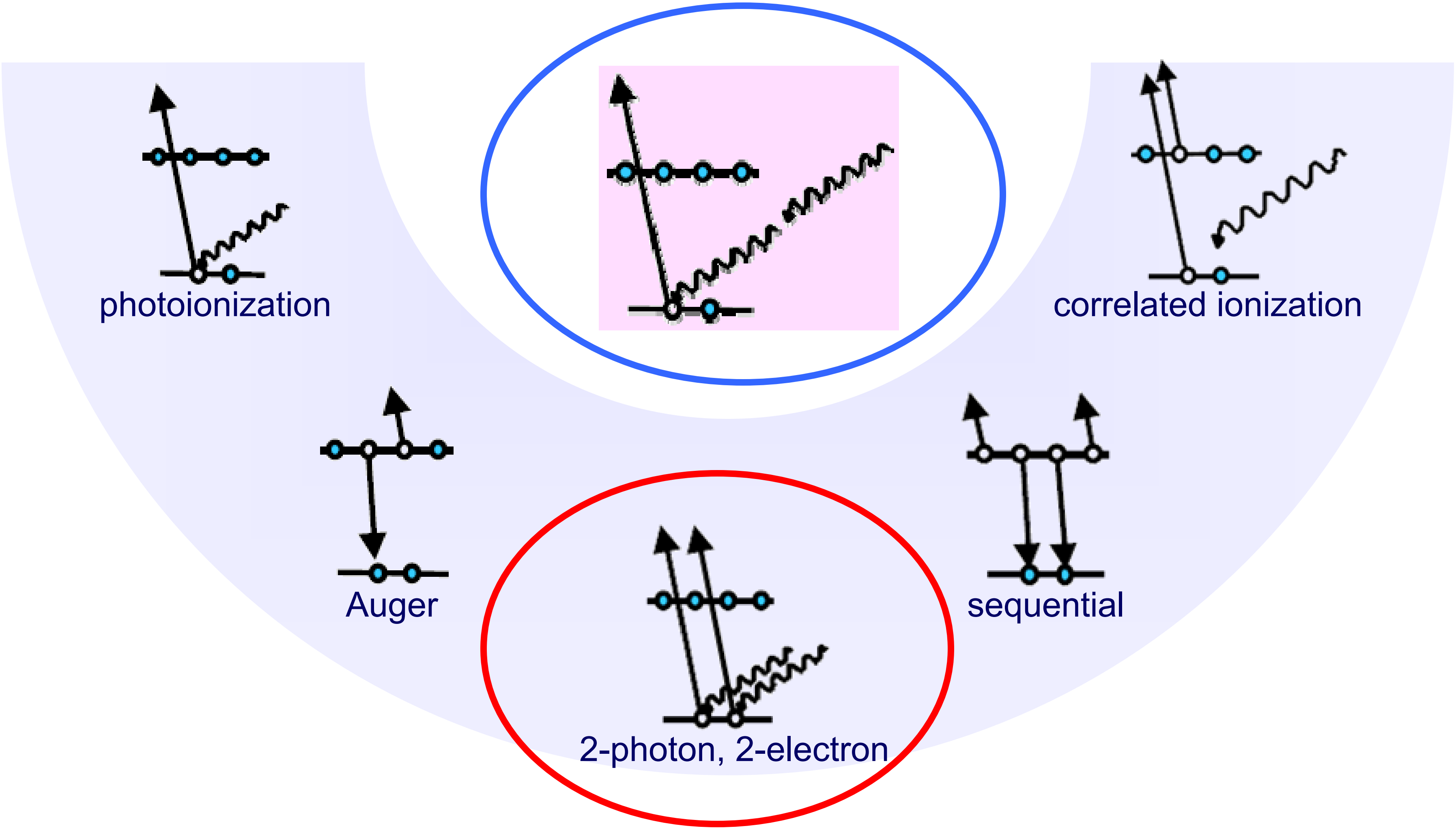


- Keldysh parameter γ <<1
- **Tunnel / over the barrier ionisation**
- Ponderomotive Energy 10 – 100 eV

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

Possible Ionization Processes @LCLS

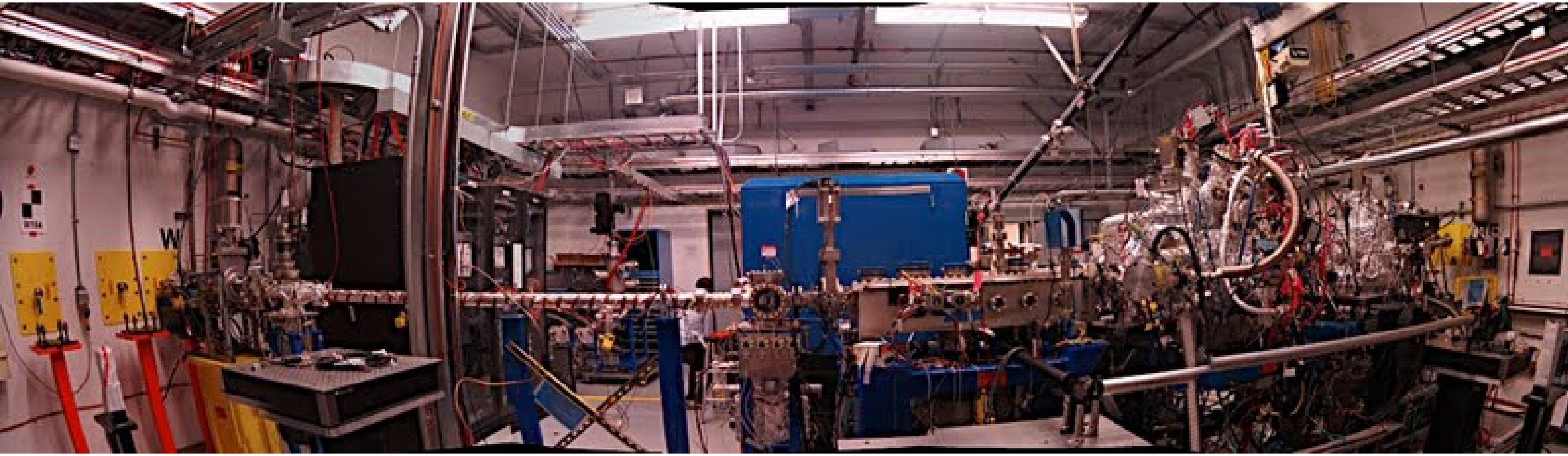
X-Ray Multiphoton Ionization

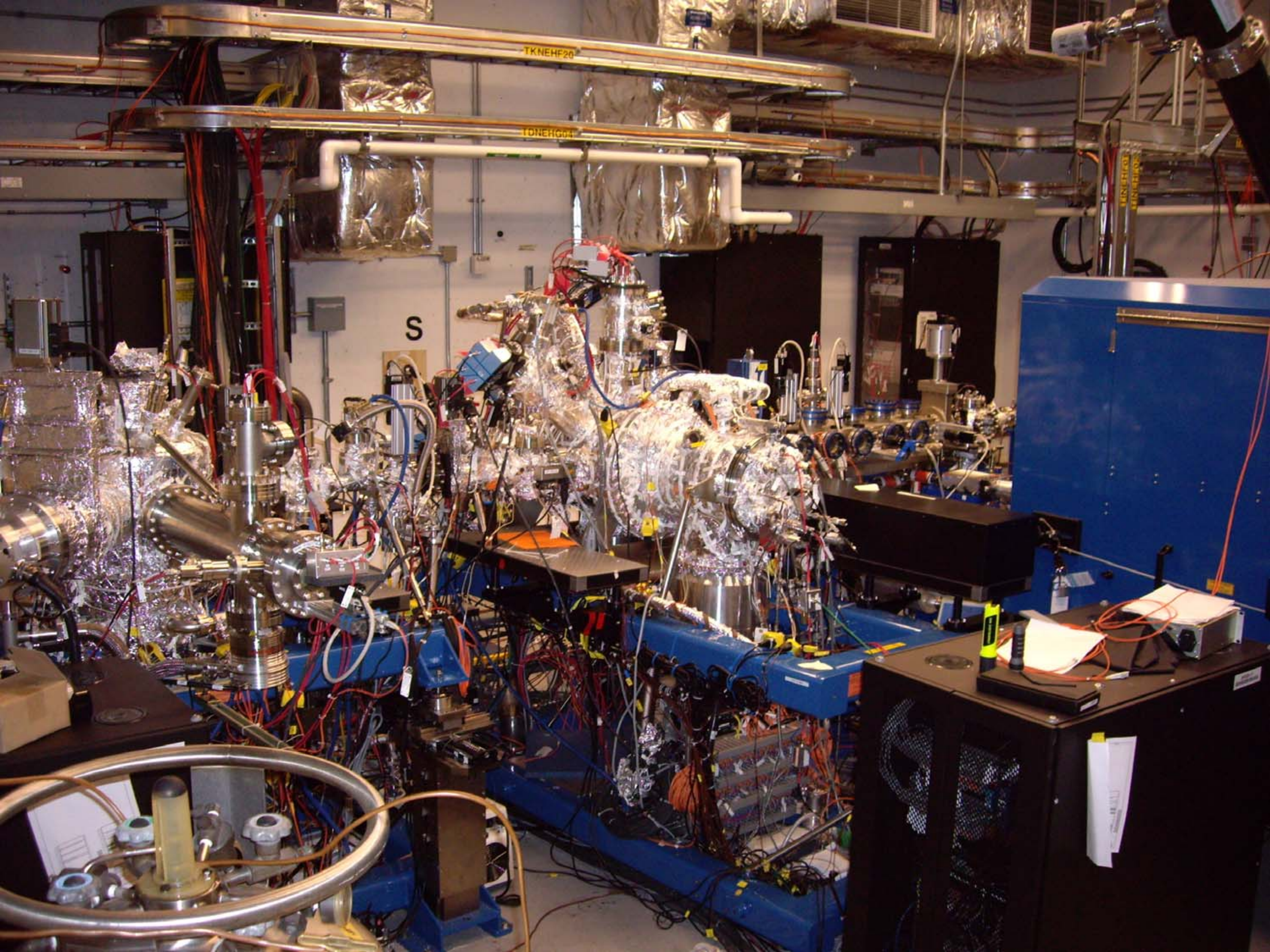



“Before”: October 2008

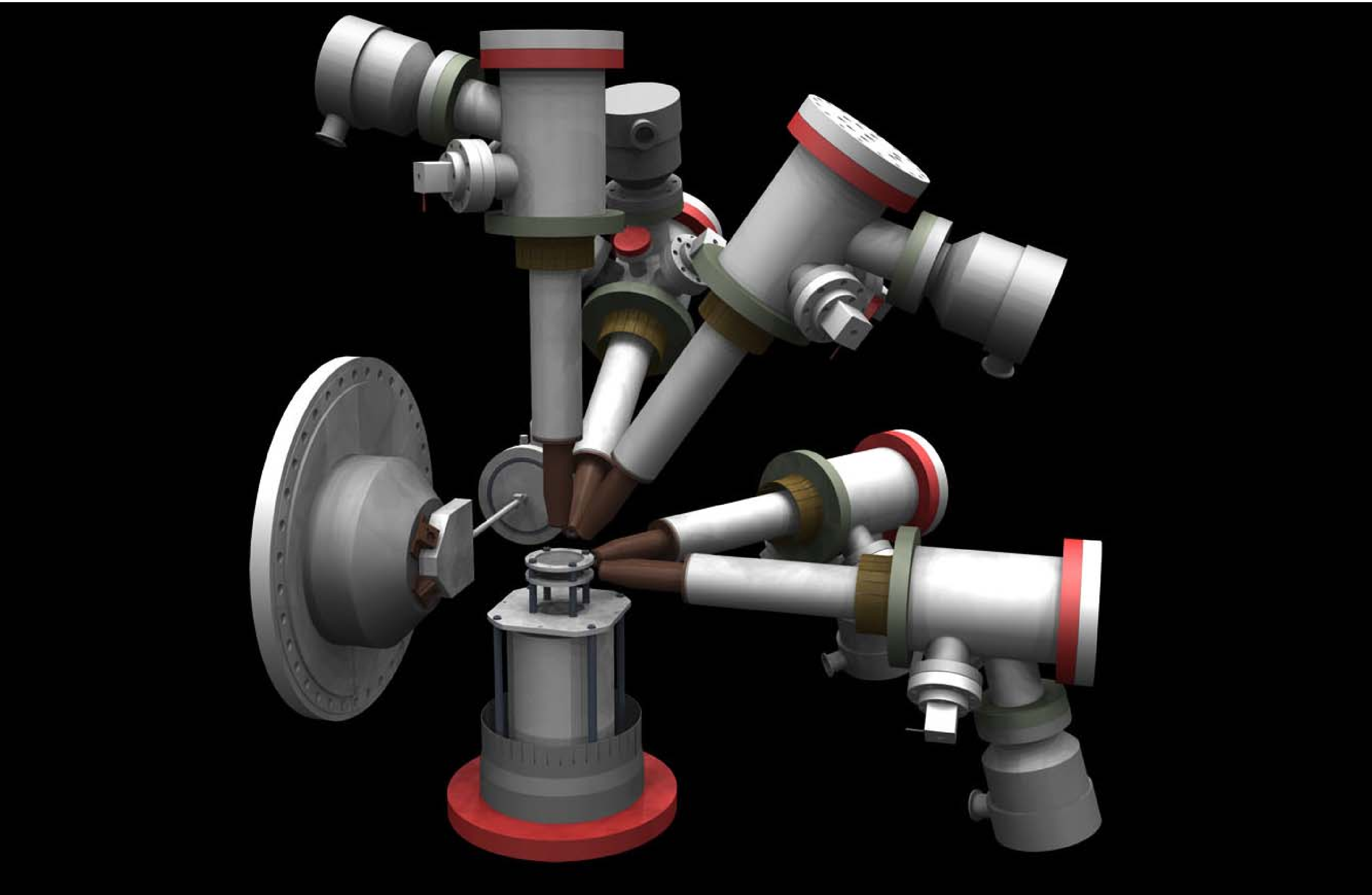
Use the LCLS High-Field Experimental System….

After: October 2009




TKNEHF20
S

AMO Instrument



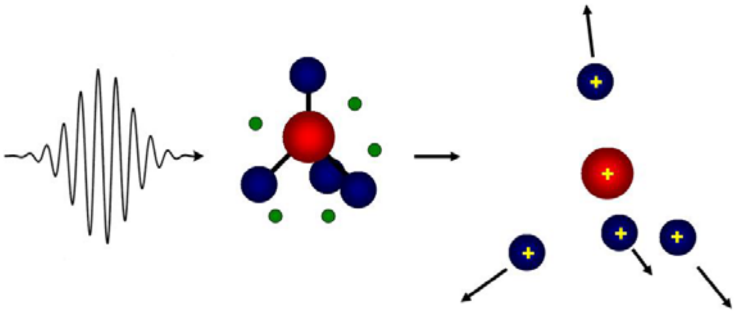

RETURN
SUPPLY
e-Vision+
RGA
mks
HFP-VIC-04
S
DO NOT TOUCH
Do Not Remove

Run#3: Molecular Collaboration I,(Oct 2009)

M. Hoener[1], L. Fang[1], O. Kornilov[2],O. Gessner[2], S.T. Pratt[3], F.Tarantelli[&], M. Gühr[4], E.P. Kanter[3], C. Bostedt[6], J.D. Bozek[6], P.H. Bucksbaum[4], C. Buth[4,7], R. Coffee[6], M. Chen[#], J. Cryan[4], L. DiMauro[5], M. Glownia[4], E. Hosler[2], E. Kukk[8], S.R. Leone[2,9], B. McFarland[4], M. Messerschmidt[6], B. Murphy[1], V. Petrovic[4], D. Rolles[10], and N. Berrah[1]

[1] Western Michigan University, Kalamazoo, MI, 49008, USA
[2] Lawrence Berkeley National Laboratory, Berkeley, CA, 94720, USA
[3] Argonne National Laboratory, Argonne, IL 60439, USA
[&] Dipartimento di Chimica, Universitadi Perugia, and ISTM-CNR, 06123 Perugia, Italy
[4] The PULSE Institute for Ultrafast Energy Science, SLAC National Accelerator Laboratory, Menlo Park, CA 94025, USA
[5] The Ohio State University, Department of Physics, Columbus, OH, 43210, USA
[6] LCLS, Menlo Park, CA, 94025, USA
[#] Lawrence Livermore National Laboratory, Livermore, C
[7] Department of Physics and Astronomy, Louisiana State University, Baton Rouge, LA, 70803, USA
[8] Department of Physics and Astronomy, University of Turku, 20014 Turku, Finland
[9] Departments of Chemistry and Physics, University of California Berkeley CA 94720, USA
[10] Max Planck Advanced Study Group, CFEL, 22761 Hamburg, Germany

GOAL of Run #3: Explore the Response and Evolution of Molecules to Single, Intense, Short, X-Ray Pulses:



N_2, CO, H_2S, SF_6

Use Ion, Photoelectron and Auger Spectroscopy

***Competition**: Multi-photon ionization, Auger relaxation*

***Competition:** Dissociation and Electronic Dynamics in Molecules*

1) Frustrated absorption in N_2 with short pulse duration

2) The formation and relaxation dynamics of Double Core Hole States

WHY are Double Core Hole States interesting??

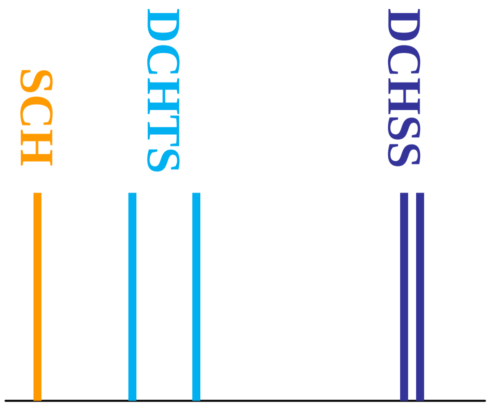
Markers Allowing Molecular Chemical Analysis

X-ray two photon photoelectron spectroscopy (XTPPS)

PRL 103, 013002 (2009) PHYSICAL REVIEW LETTERS week ending 3 JULY 2009

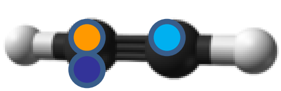
X-Ray Two-Photon Photoelectron Spectroscopy: A Theoretical Study of Inner-Shell Spectra of the Organic Para-Aminophenol Molecule

Robin Santra,[1,2,*] Nikolai V. Kryzhevoi,[3] and Lorenz S. Cederbaum[3]

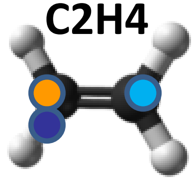


Binding energy of **C** K-shell electron

C2H2



C2H4



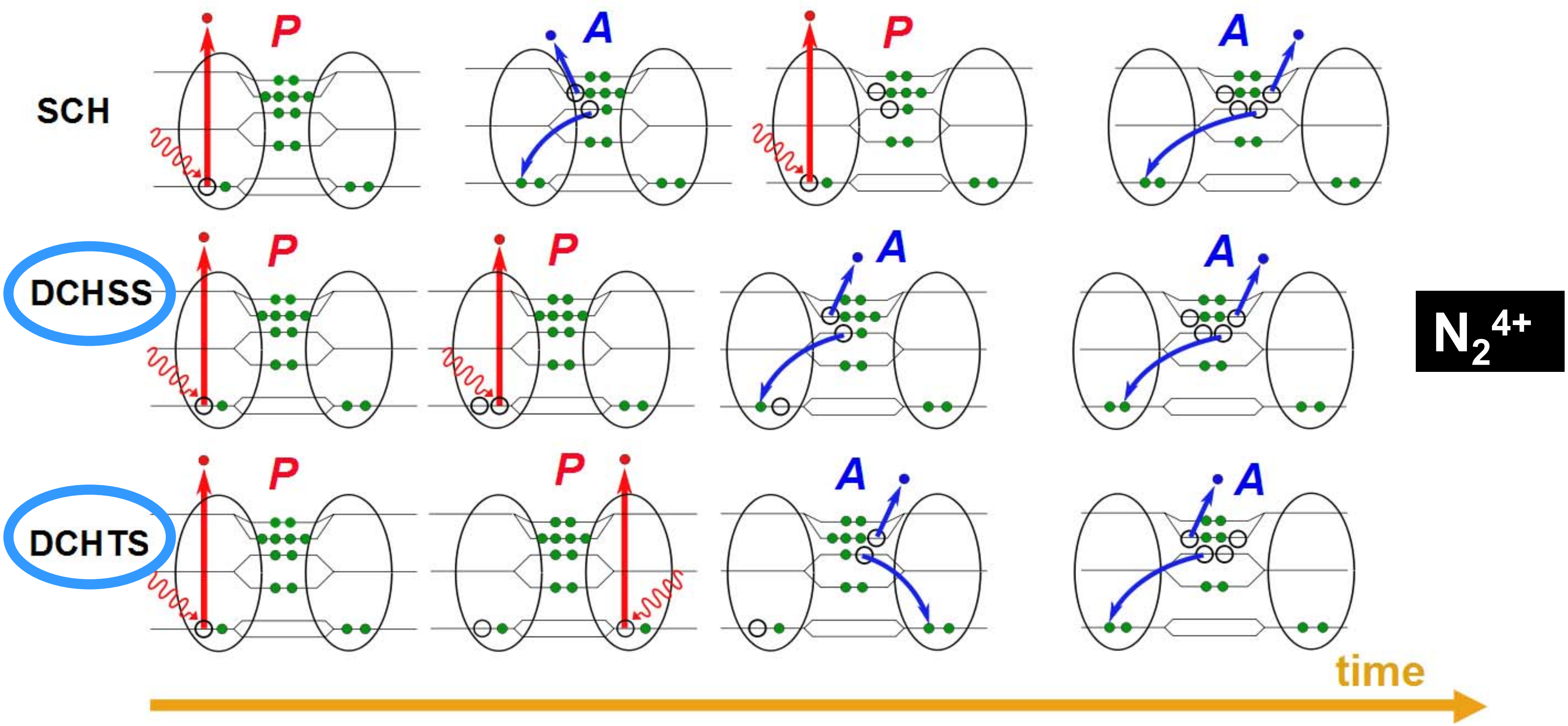
L. S. Cederbaum *et al.*, J. Chem. Phys. (1986).

- o **Single core hole (SCH)**
  - Site specific.
  - *Insensitive* to the chemical environment of the core holes.
- o **Double Core Holes on Single atomic Site (DCHSS)**
- o **Double Core Holes on Two atomic Sites (DCHTS)**
  - *Sensitive* to the chemical environment of core holes.
  - XTPPS: New chemical analysis tools.

X-ray Induced Sequential Multiple Ionization in N_2

During ONE X-Ray Pulse: Multi-Cyclic Core hole Phot.+Auger Decay

Pulse Duration >Auger Decay (6.4 fs)



Before Auger Decay

Possible Ionization and Dissociation Pathways of N_2 with 1.0 keV @ LCLS

During the same X-Ray Pulse

- $N_2 + h\nu \rightarrow N_2^+ + e^-_v$ **Valence Photoionization**
- $N_2 + h\nu_1 \rightarrow N_2^+ + e^-_p \rightarrow N_2^{2+} + e^-_p + e^-_A$ **Auger decay**

  Asymmetric Dissociation $N_2^{2+} \rightarrow N^{2+} + N$

  Symmetric Dissociation $N_2^{2+} \rightarrow N^+ + N^+$

N, N^+, N^{2+} absorb more hν from the same x-ray pulse → **PA** → N^{2+}, N^{3+}, N^{4+} → **PA** → N^{3+}, N^{4+} …

- $\mathbf{N_2^{2+}} + h\nu_2 \rightarrow N_2^{4+} + e^-_p + e^-_A$

  $\mathbf{N_2^{4+} \rightarrow N^{3+} + N^+}$

  DCH (PPAA) or SCH (PAPA)

  $\mathbf{N_2^{4+} \rightarrow N^{2+} + N^{2+}}$

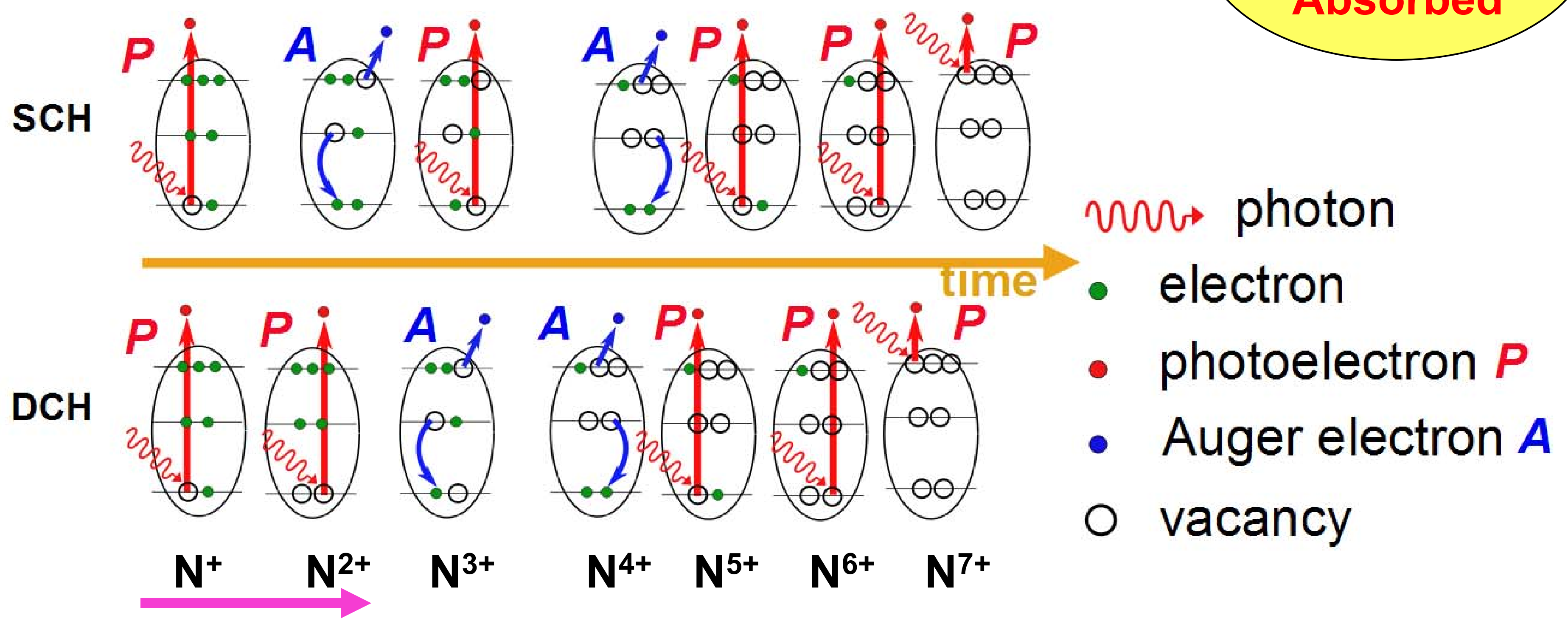
Increasing Molecular Charge → Transition from Molecular to Atomic Ionization

X-ray Induced Sequential Multiple Ionization in N

During ONE X-Ray Pulse: Multi-Cyclic Core Photoi.+ Auger Decay

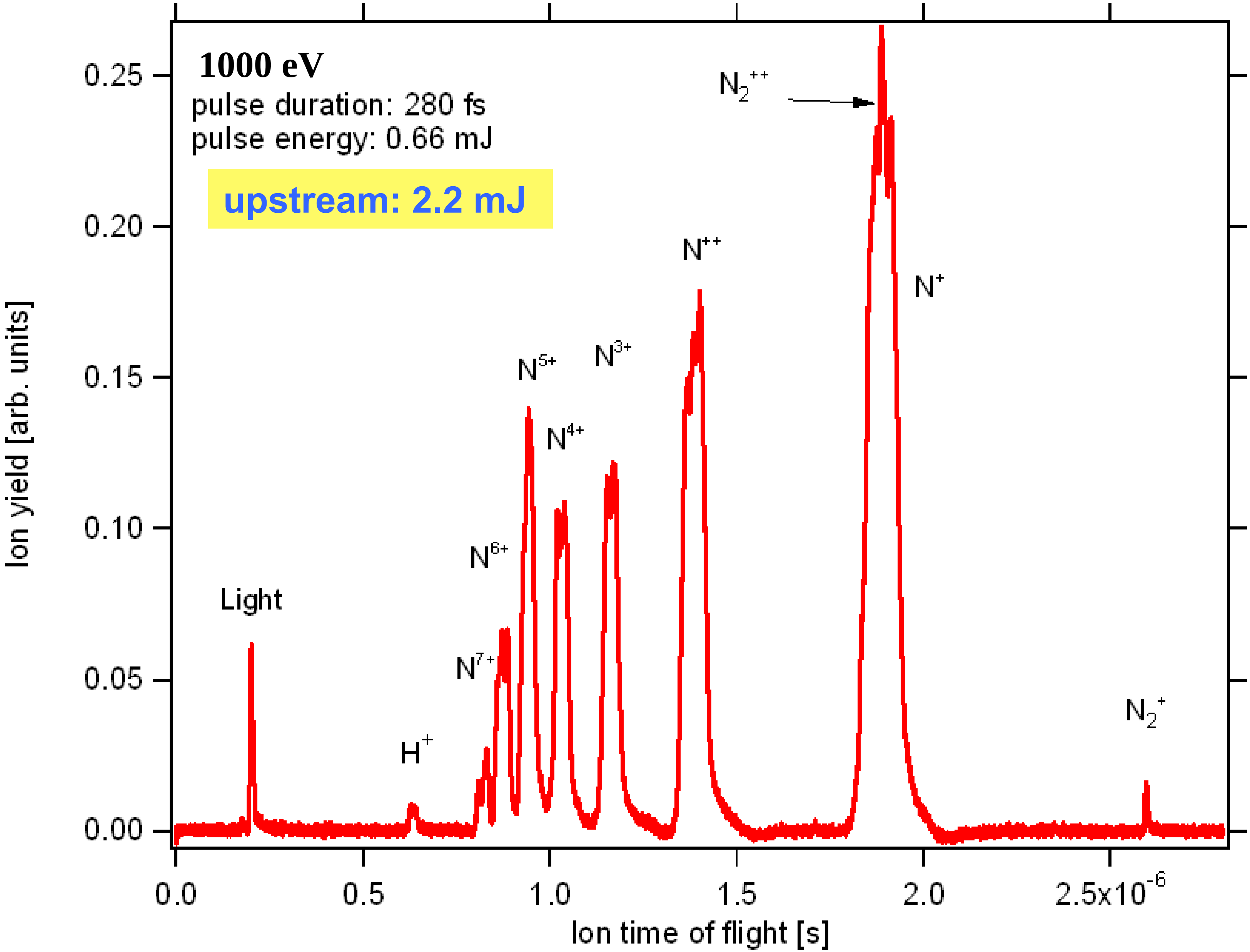
5 Photons Absorbed

Pulse duration > Auger Decay:6.4 fs

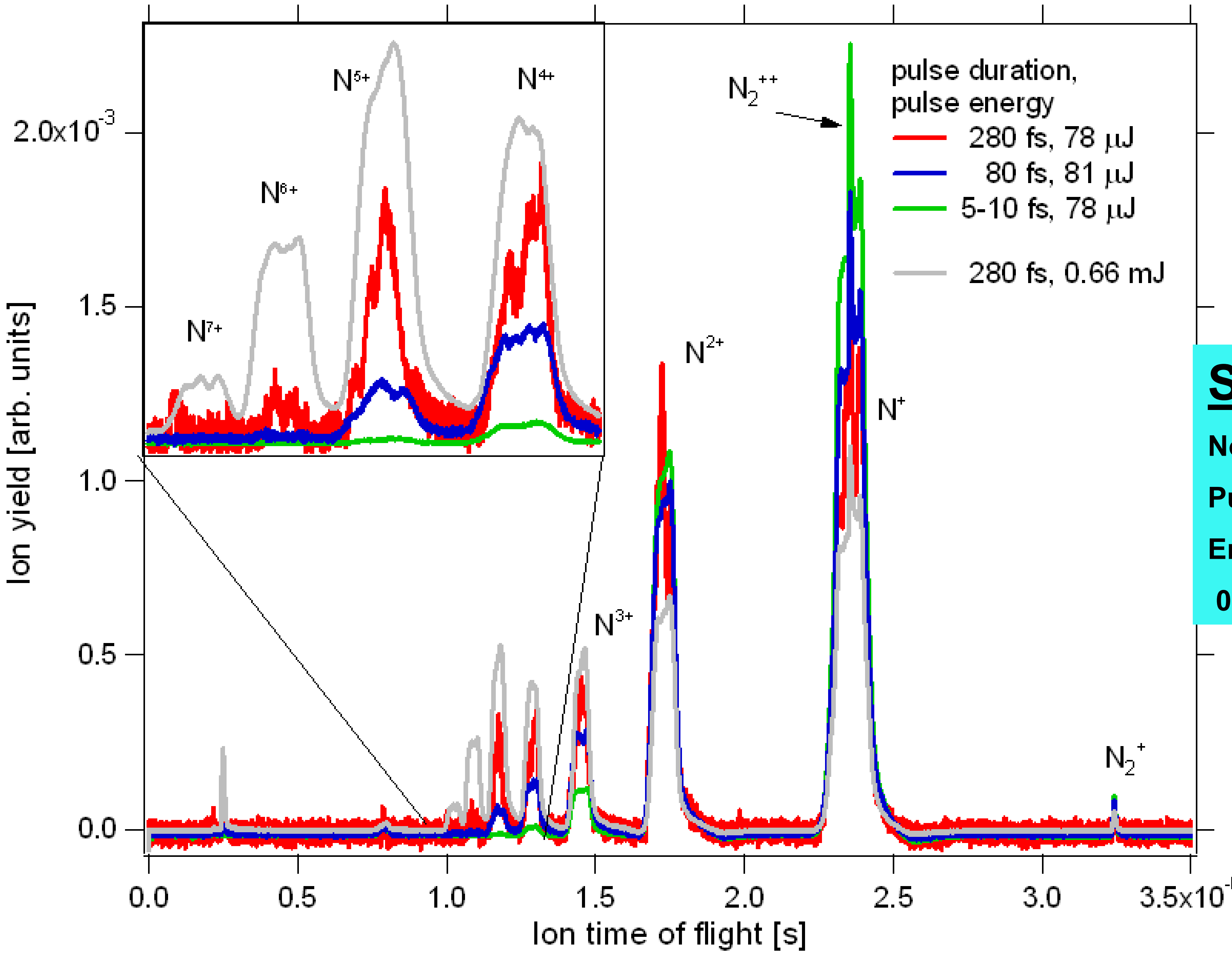


Pulse duration <Auger Decay:
HOLLOW ATOM

X-ray Induced Multiple Ionization of N_2



Photoionization of N_2 as a function of Pulse Duration

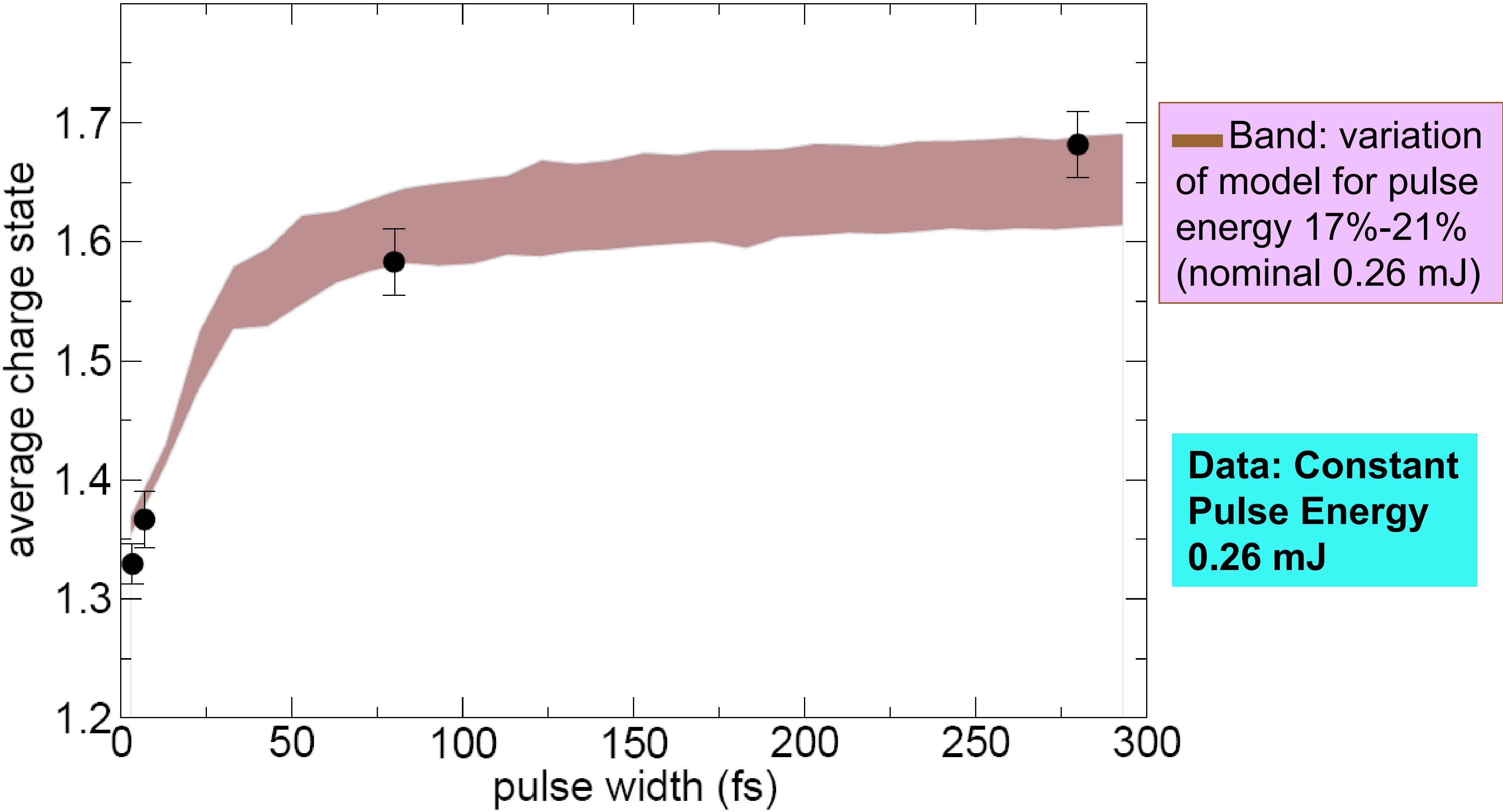


Same

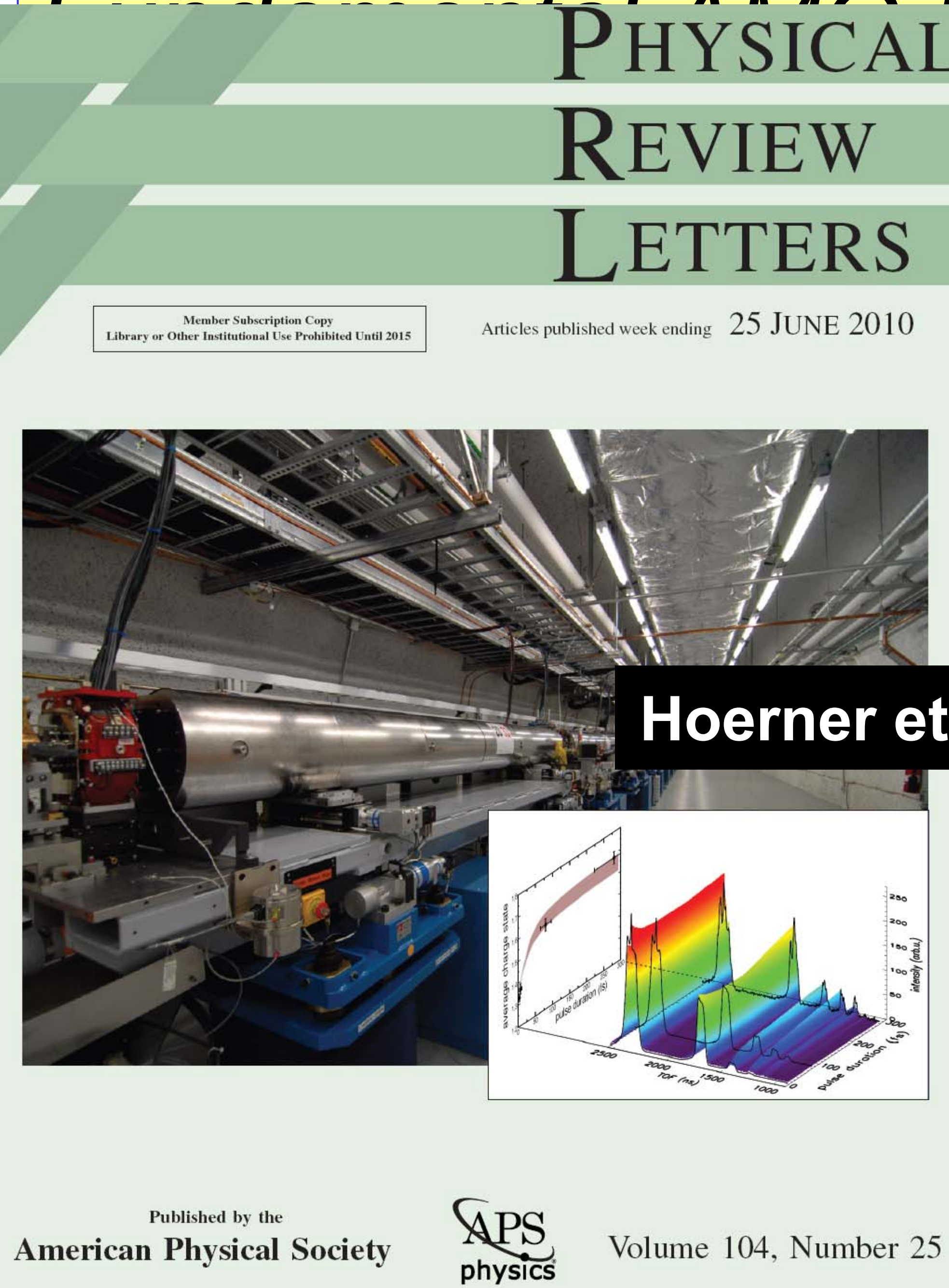
Nominal Pulse Energy 0.26 mJ

Frustrated Absorption/Transparency @ Short X-FEL Pulses; Minimizes Electronic Damage

$$q_{av}(\tau) = \sum_{i=1}^{7} N_i(\tau) q_i \Big/ \sum_{i=1}^{7} N_i(\tau)$$



Result Impact:
Structure
molecules

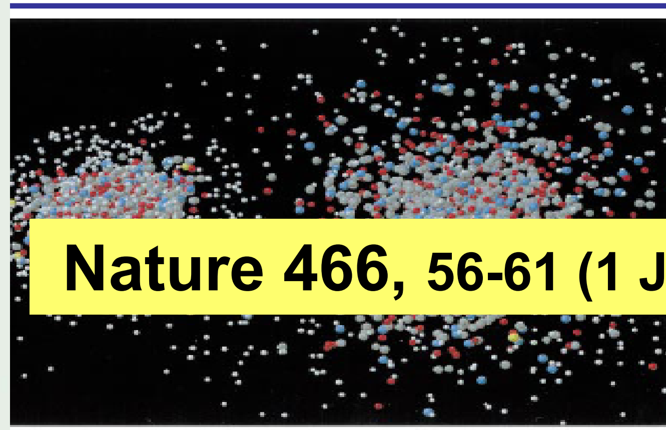


Frustrated Absorption
Transparency

le before it can be mapped.

Hoerner et al. PRL 104, (June 25th 2010)

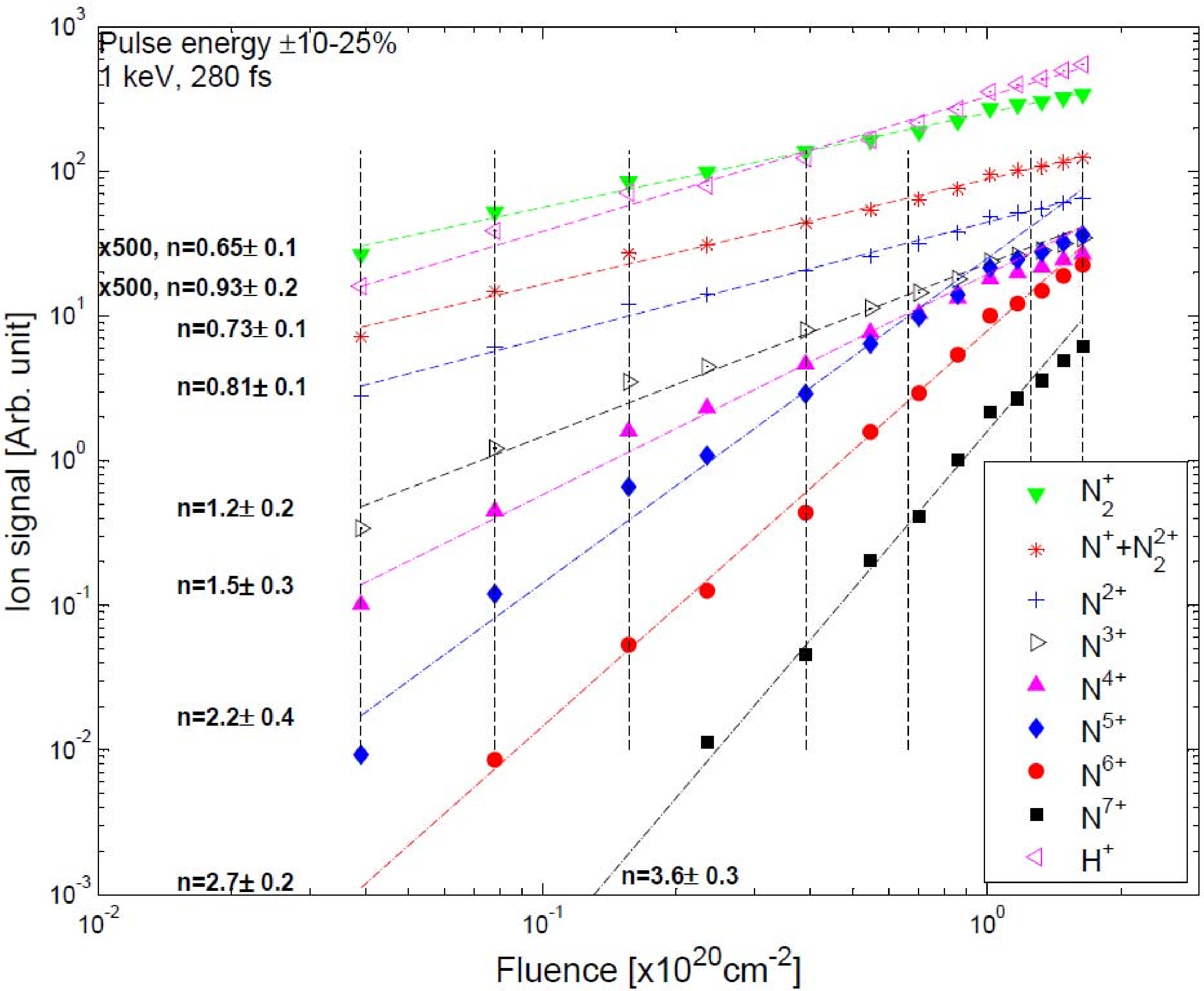
nb Explosion during Scattering



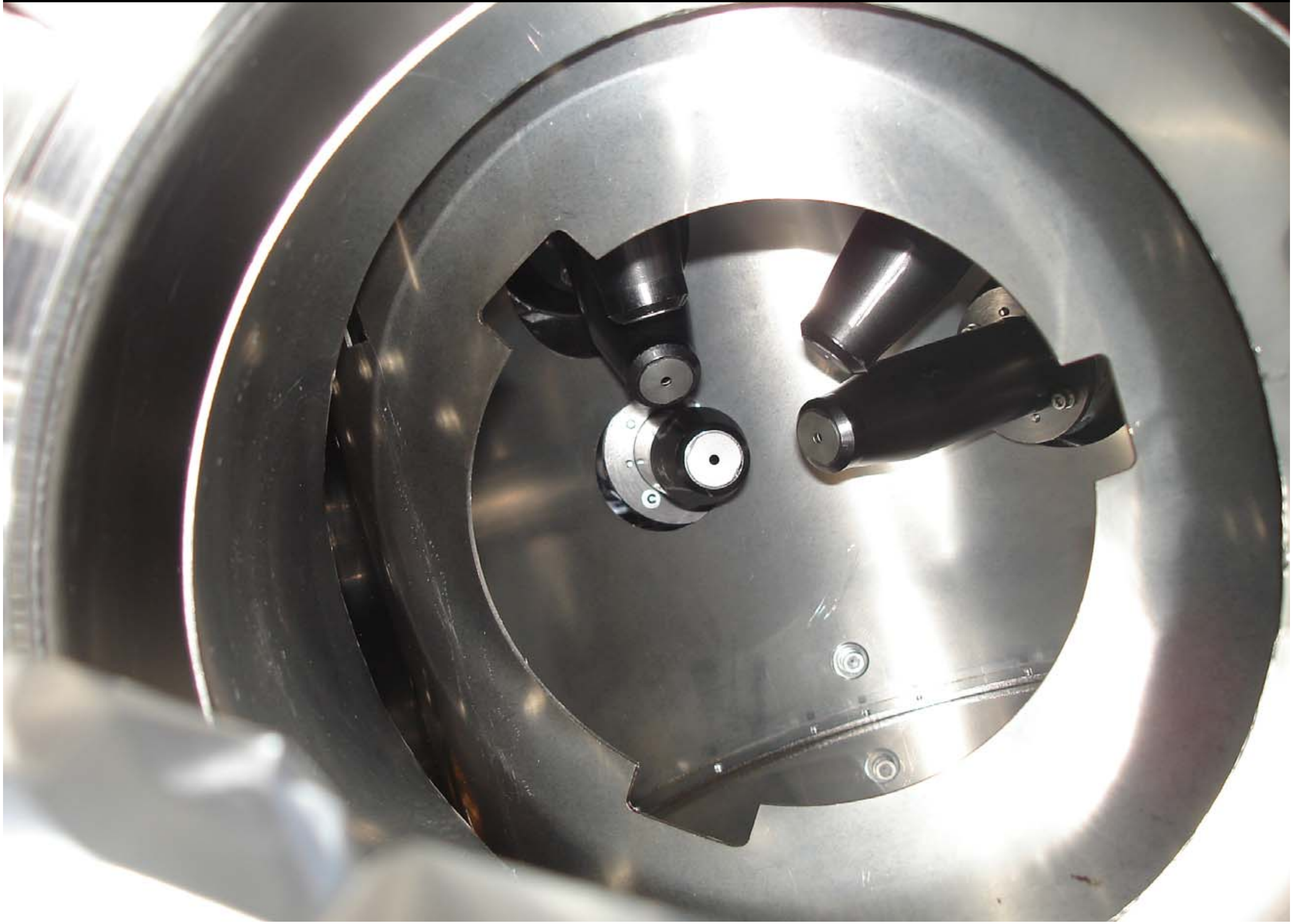
Nature 466, 56-61 (1 July 2010).

t=−2fs t=2fs t=5fs t=10fs t=20fs t=50fs

N_2 Sequential Multiphoton Ionization:#Pulse Energy

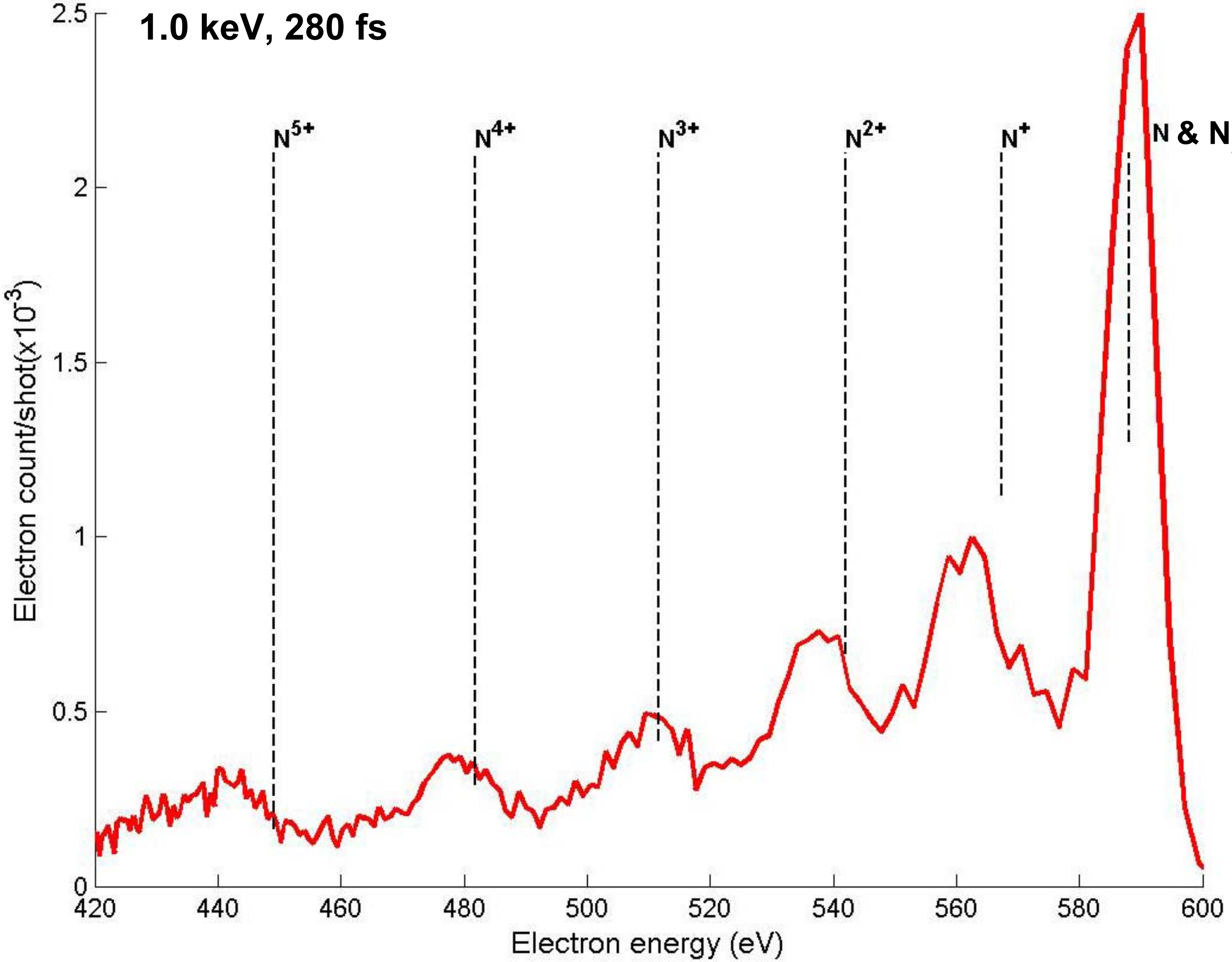


Probing Double Core hole in N_2



N_2 Sequential Multiphoton Ionization PES spectrum

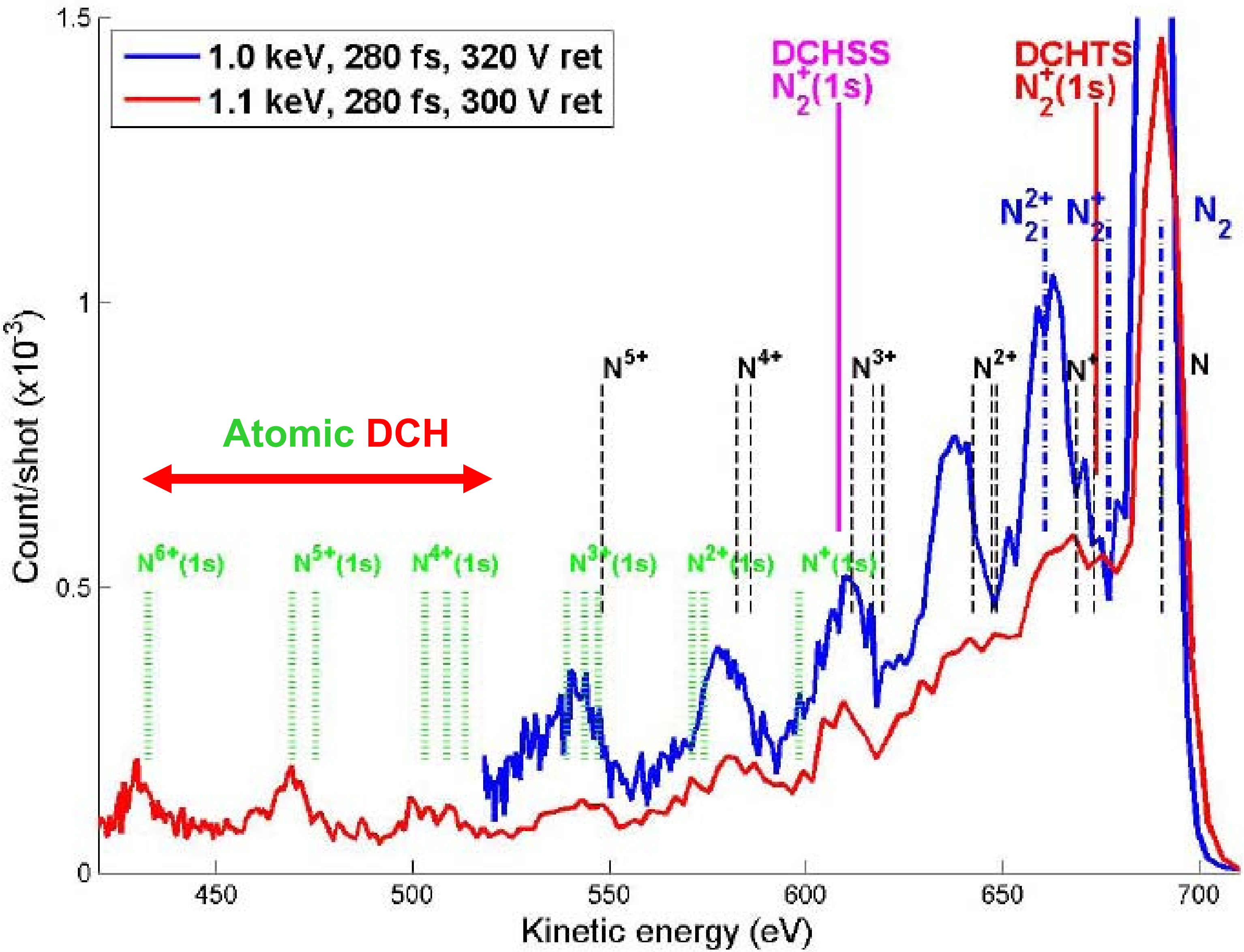
--- Calculated M.Chen/Tarantelli. SCH, N^{q+}: initial charge states with q valence holes



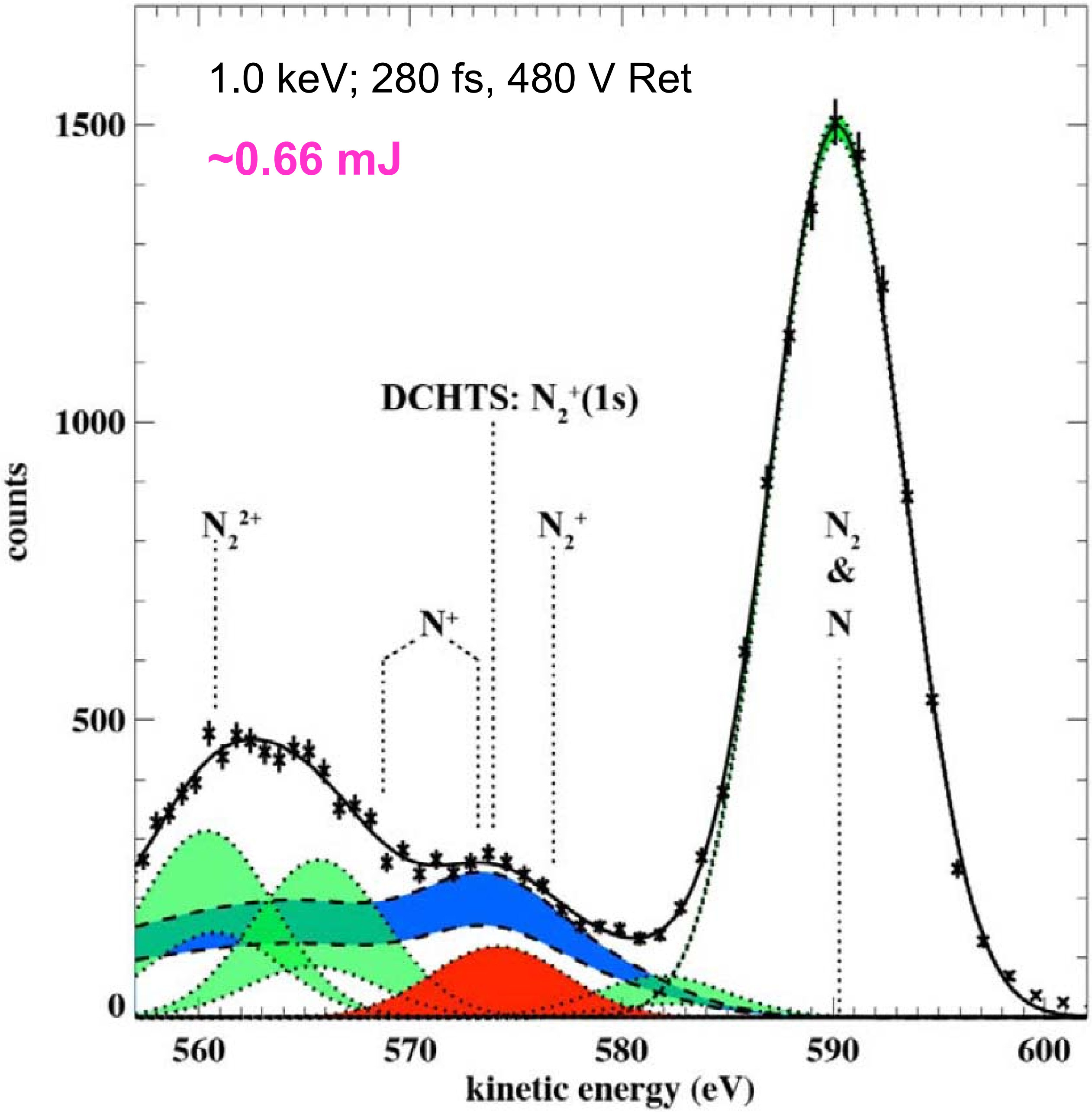
▪▪▪▪ SCH: N_2, N_2^+, N_2^{2+},

--- **N^{q+},** SCH, charge states with n valence holes

--- **N_{1s}^{q+}, DCH, charge states with 1s hole and q-1 valence holes**



Double Core Hole Two Site (DCHTS)



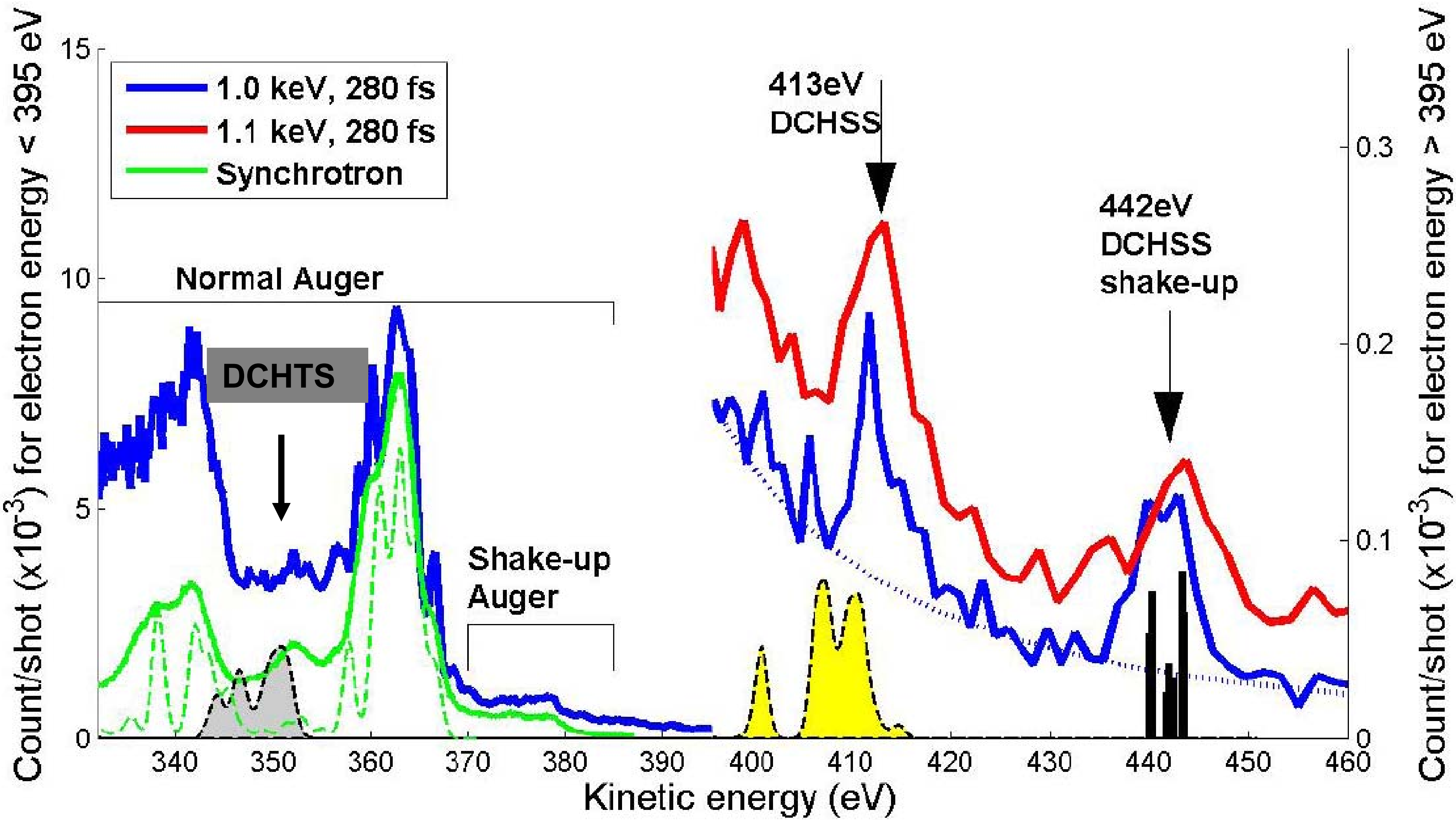
Single Ionization Regime

Main line + Shake up/off ONLY!

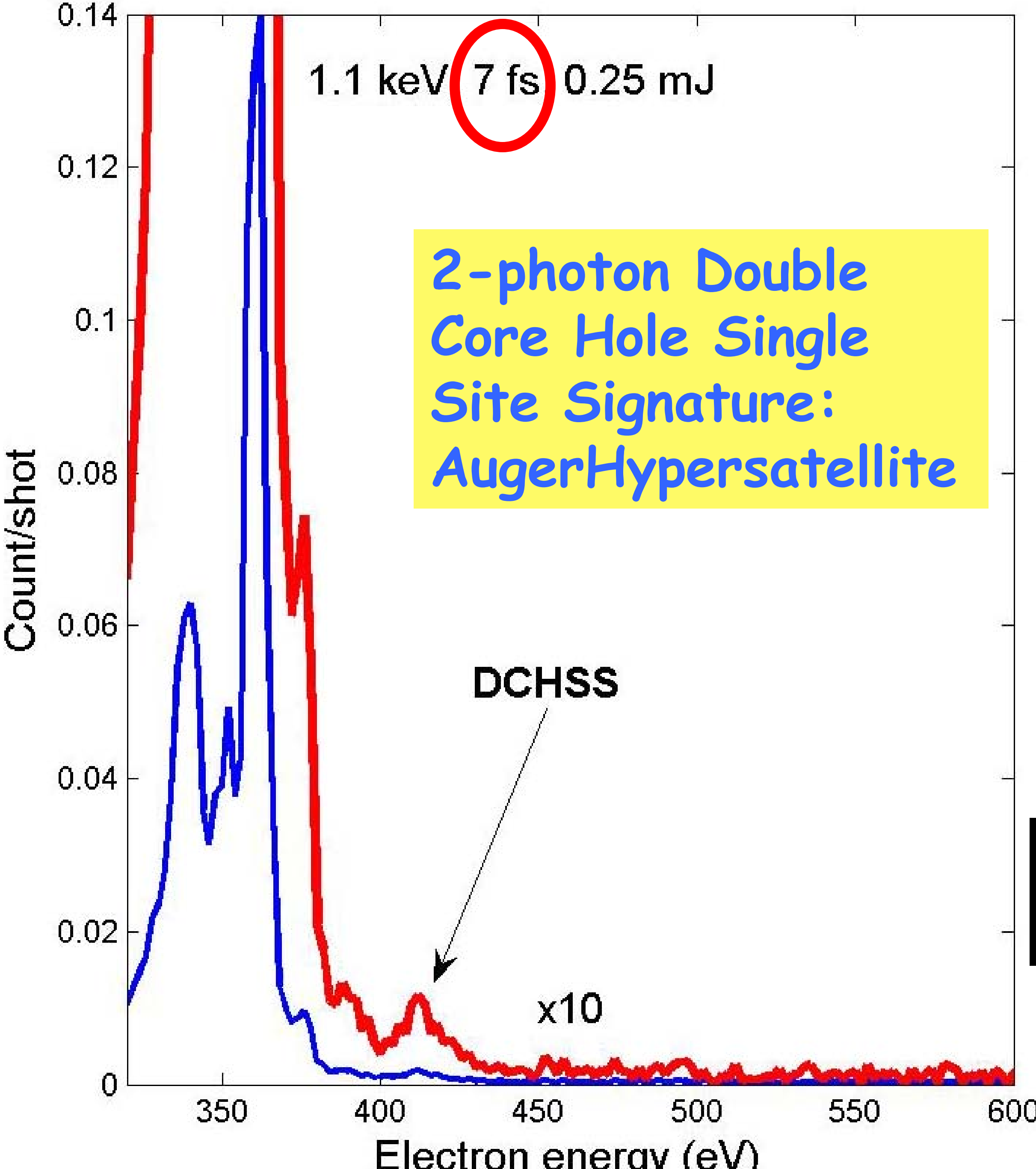
Single-photon Shake up/off; Shape& range of uncertainty, Svensson. JPB'92; Kaneyasu JPB '08

DCHTS: Upper limit estimate 4% of the main line.

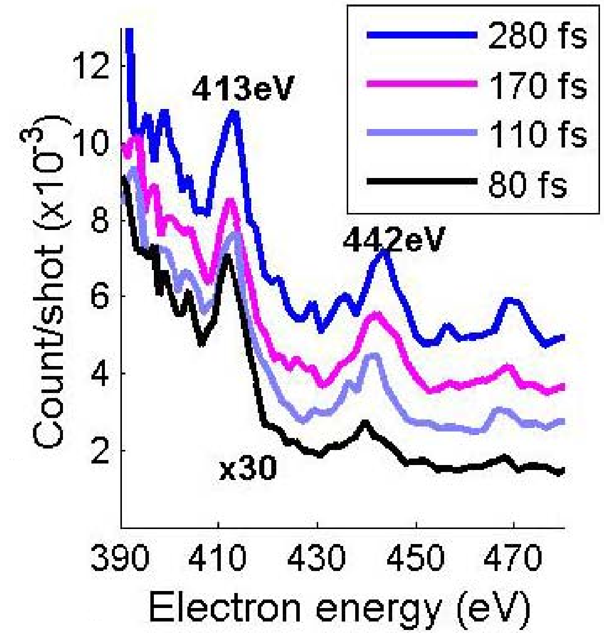
Two-Photon Double Core Hole Single Site:
Auger Hypersatellite



▪▪▪▪▪▪ *ab-initio* Green's function calculations; F. Tarantelli



2-photon Double Core Hole Single Site Signature: AugerHypersatellite



Reproducibility of DCHSS

Fang et al. PRL **105**, 083005 (2010)

Cryan et al. PRL **105**, 083004 (2010)

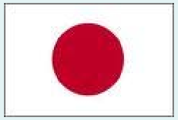
LCLS Molecular Collaboration II (Oct 2010)

We have measured <u>one-site</u> and <u>two-site double</u> core hole photoelectron spectra and Auger electron spectra of N_2, CO, N_2O, and CO_2.

Tashiro/Ehara (Japan) have calculated Auger spectra of CO.

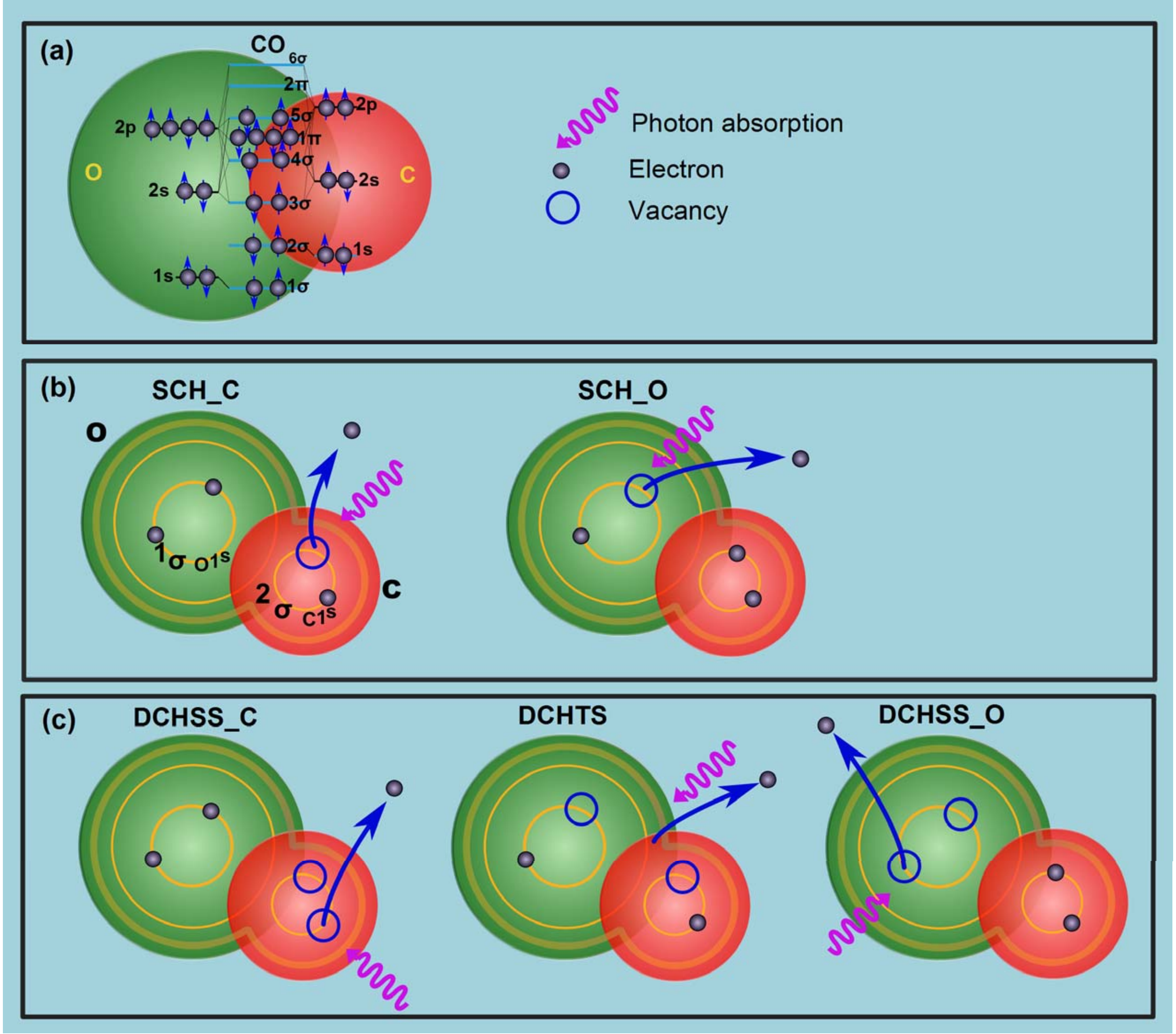
M. Larsson**, P. van der Meulen, P. Salen, **R. Feifel** et al.; **Sweden

K.C. Prince,** R. Richter, F. Tarantelli; **Italy



K. Ueda,** M. Tashiro, M. Ehara et al.; **Japan

N. Berrah**, Fang, Osipov, Murphy, E. Kukk et al.; **USA


(a)
CO
6σ
2π
5σ
1π
4σ
3σ
2σ
1σ
2p
2s
1s
O
C
Photon absorption
Electron
Vacancy
(b)
SCH_C
SCH_O
O
C
1σ
O1s
2σ
C1s
(c)
DCHSS_C
DCHTS
DCHSS_O

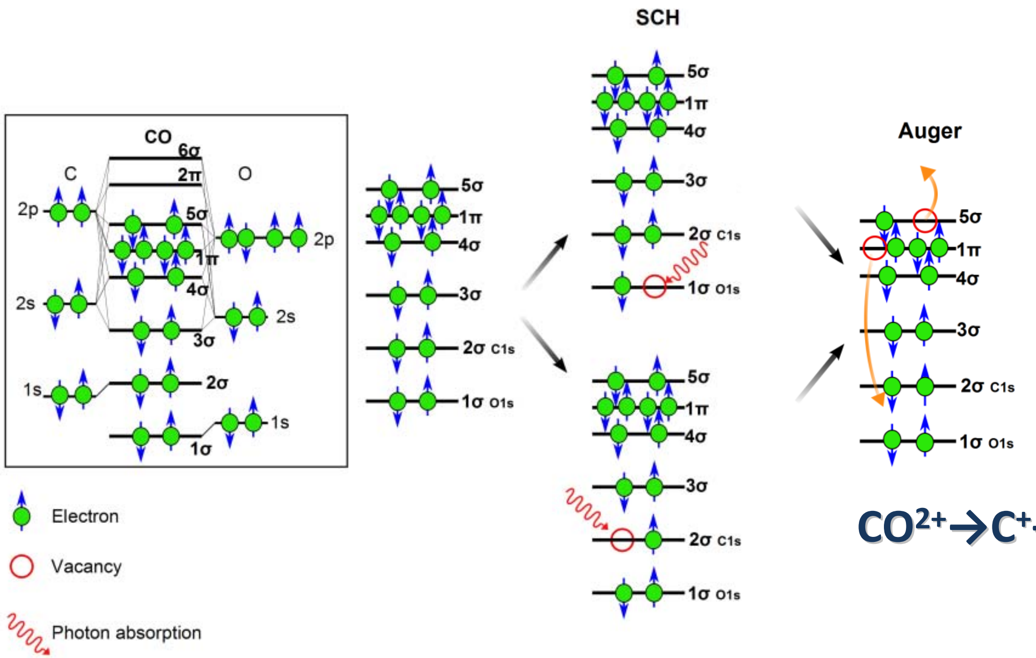
X-ray Induced Sequential Multiple Ionization: CO

Conventional source: synchrotron X-ray

Intense FEL short pulse at LCLS:

500-2000 eV, sub 10fs-300fs, 10^{18}W/cm^2

CO



$CO^{2+} \rightarrow C^{+} + O^{+}$

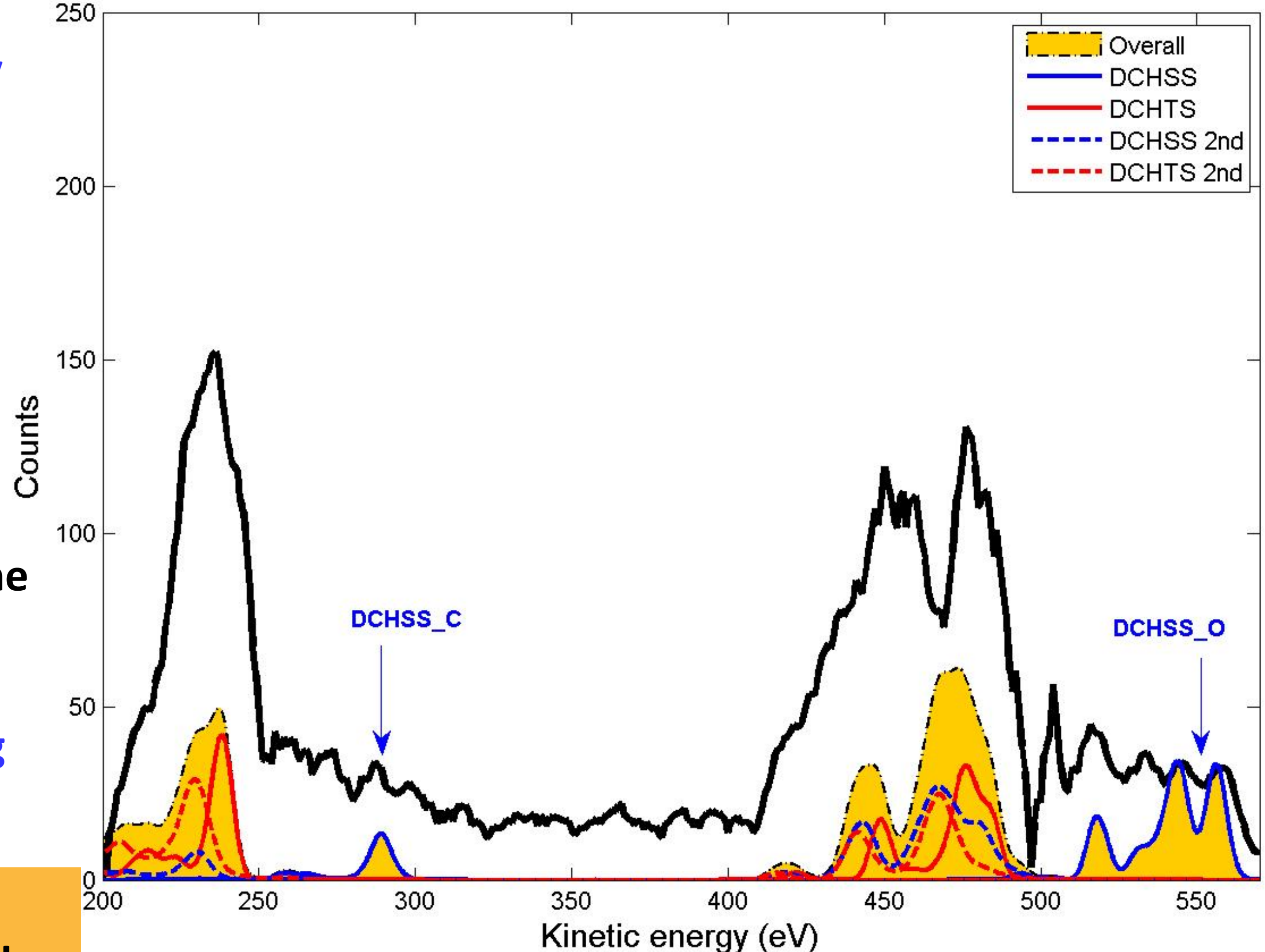
- FEL exposure → Sequential absorption of X-ray photons
→ highly charged ions.

Double Core Holes Ionization via Auger-e Spectroscopy

Low intensity beam → mostly single photon processes.

High intensity beam → multiple ionization via *sequential multiphoton absorption* + single photon processes.

The difference between the spectra of high and low intensity – multiphoton processes alone, excluding single photon processes.



700 eV, 10-20 fs, ~10^4 photon/Å^2/pulse, ~10^{18} W/cm^2

Comparison between the experimental results and the theoretical results indicates the creation of DCHTS and DCHSS.
Theory: ***M. Tashiro, M. Ehara***

Berrah et al. PNAS, 108, 16912 (2011).

Preliminary: DCH via photoelectron spectroscopy

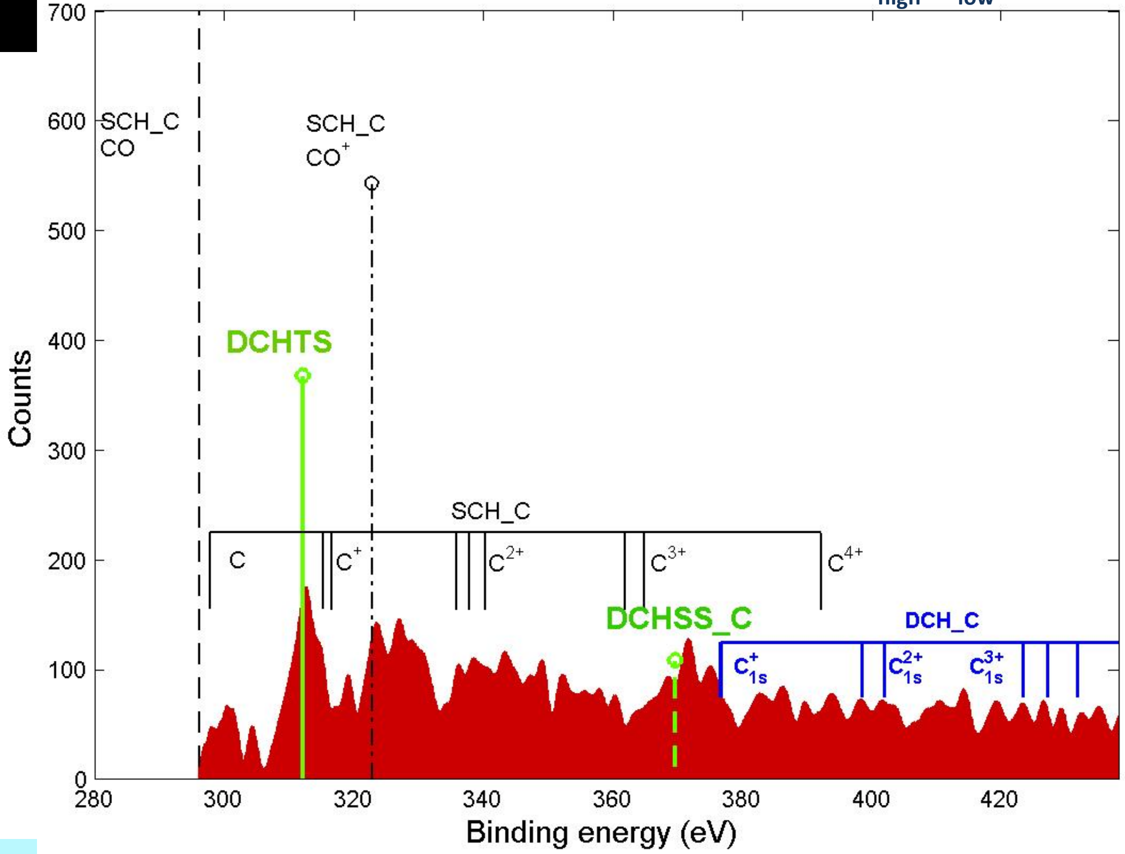
Difference of the Focused (high intensity) and Defocused (low intensity) Spectra – multiphoton processes, including DCHs.

Unambiguous observation of DCHTS in a molecule.

Experimental and theoretical binding energies in good agreement

Theory*	Experiment
SCH 298.2 eV	296.5 eV ± 0.5 eV
DCHSS 369.6 eV	371.4 eV ± 3.5 eV
DCHTS 314.2 eV	312.8 eV ± 0.7 eV
DCHSS - SCH 71.4 eV	74.9 eV ± 4.0 eV
DCHTS - SCH 16.0 eV	16.3 eV ± 1.2 eV

700 eV, 10-20 fs, ~10^4 photon/Å^2/pulse, ~10^{18} W/cm^2, I_{high}/I_{low} = ~300



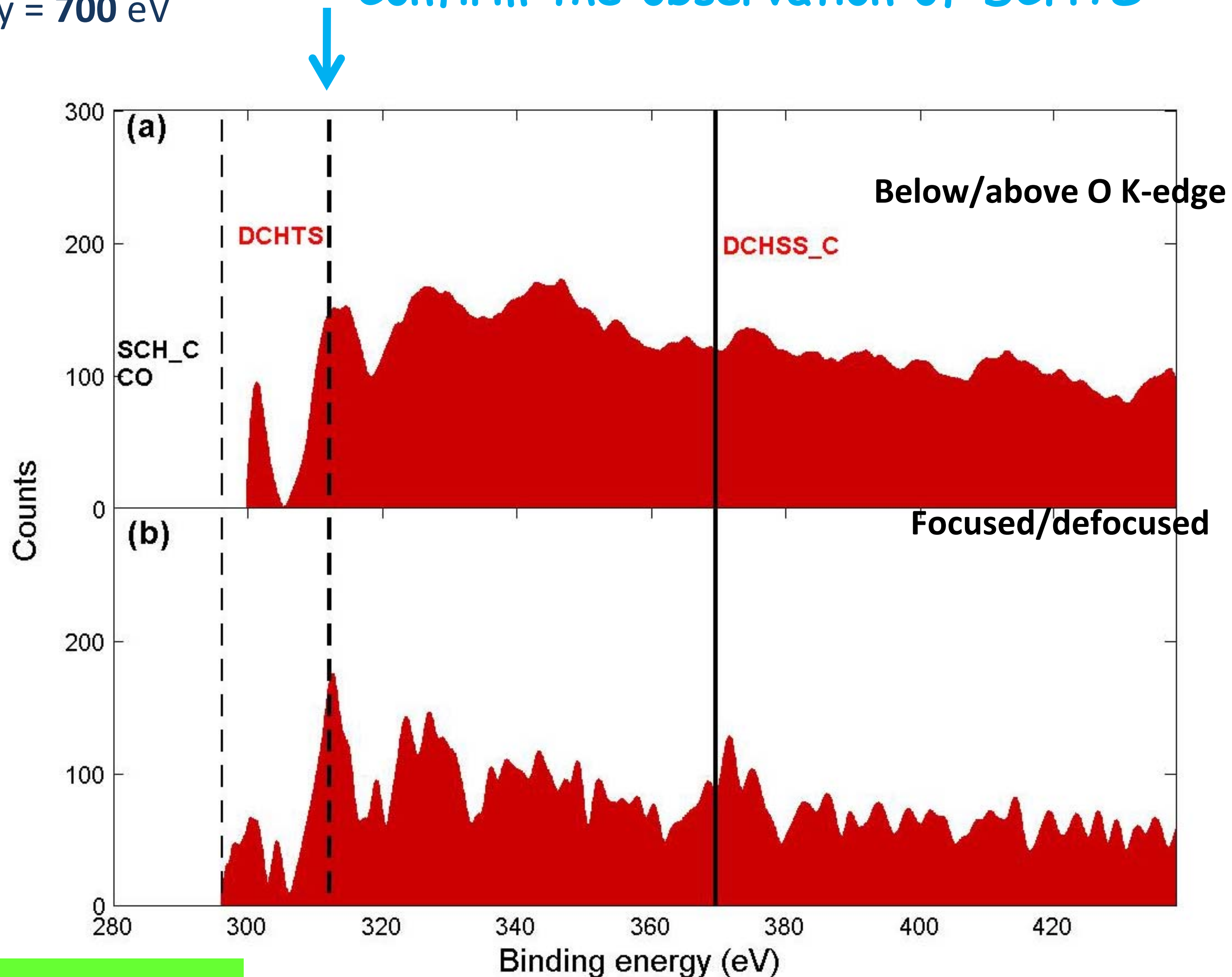
* M. Tashiro, *et al.*, J. Chem. Phys., **132**, 184302 (2010).

Confirmation of DCHTS: below/above O K-edge photoelectron spectra

Below: Photon energy = **500** eV
Above: Photon energy = **700** eV

Difference spectrum
→ DCHTS (C)

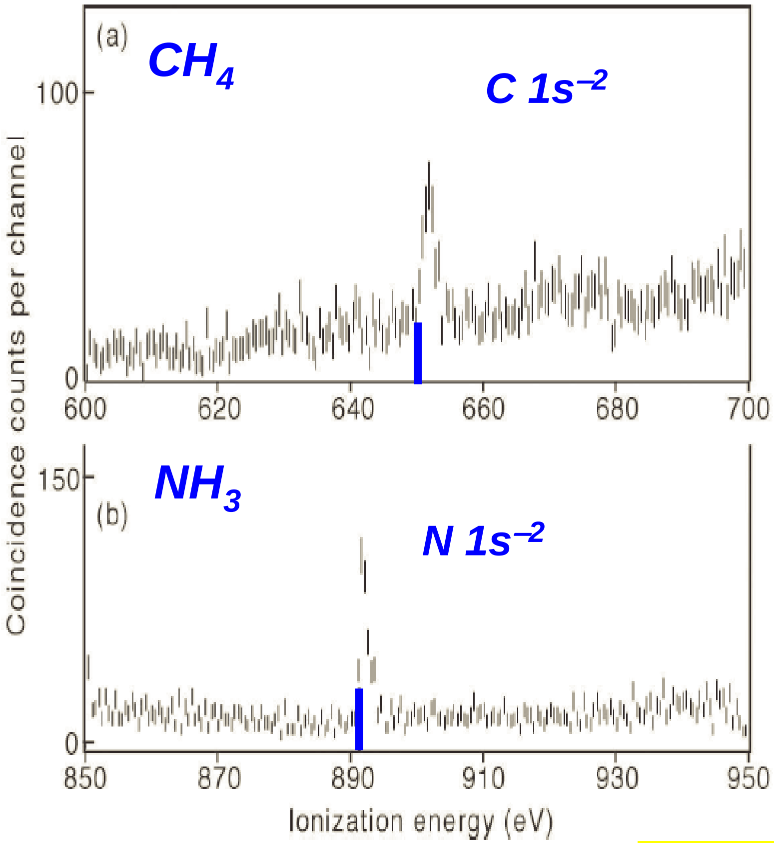
Confirm the observation of DCHTS



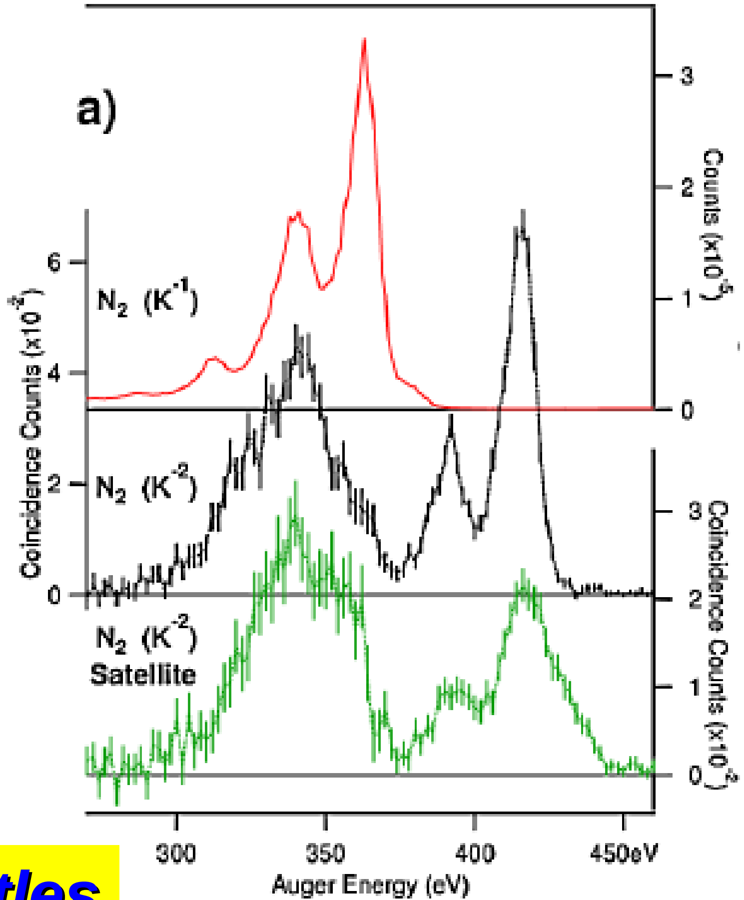
PNAS, 108, 16912 (2011).

Single photon- Double Core Hole Single Site using *Synchrotrons & Efficient Multiple Coincidence* Technique

*Eland, Tashiro, Linusson,Ehara, Ueda, and Feifel PRL **132** 184302 (2010).*



*Lablanquie, Penent, Eland, Ito et al., PRL **106**, 063003 (2011).*



Magnetic Bottles

Present and Furture Plans:

2011:

Feifel et al., *Proposal to measure DCHTS with a newly built* ***magnetic bottle*** *electron spectrometer and a* ***covariance*** *technique*

Prince et al*: Proposal to use the above technique to study and measure DCHTS in* ***biomolecules***

2012: Berrah et al. *Use above technique to investigate* ***clusters***

N. Berrah, L. Fang, B. Murphy, T. Osipov *(USA);* ***E. Kukk*** *(Finland)*

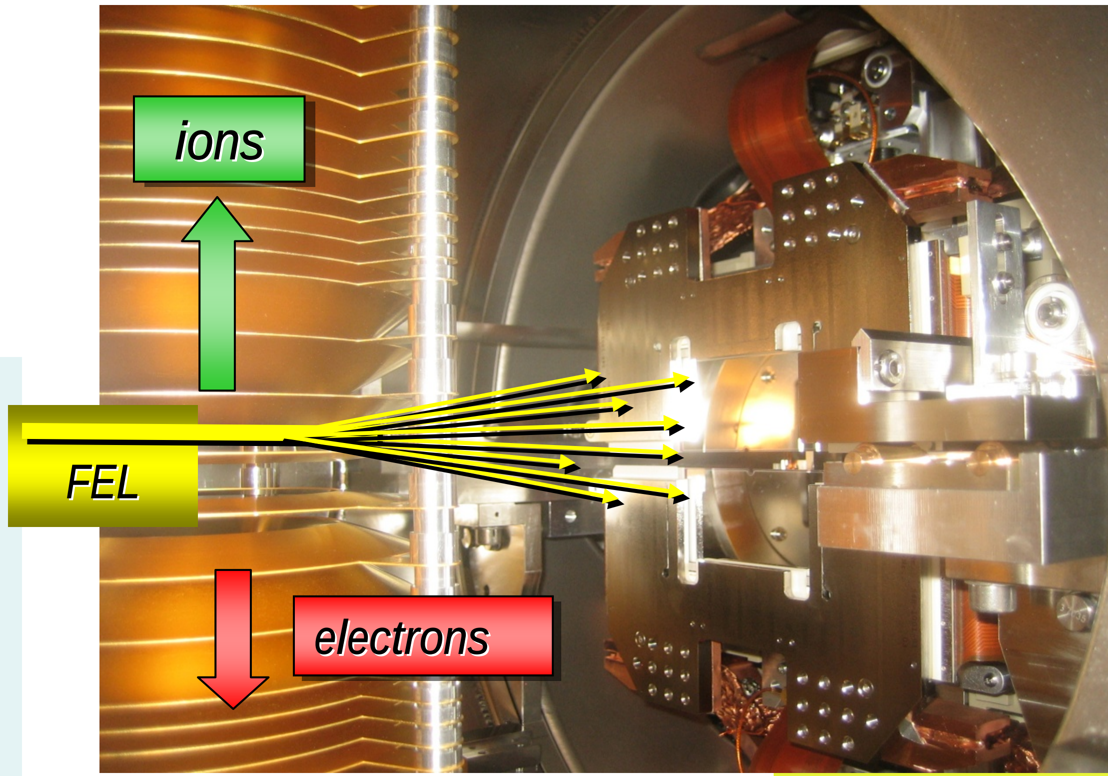
R. Feifel, M. Larsson,*et al.(Sweden),* ***J.H.D. Eland*** *et al. (UK)*

K.C. Prince, L. Avaldi, F. Tarantelli *et al.(Italy)*

K. Ueda, O. Takahashi, M. Tashiro, M. Ehara *et al. (Japan)*

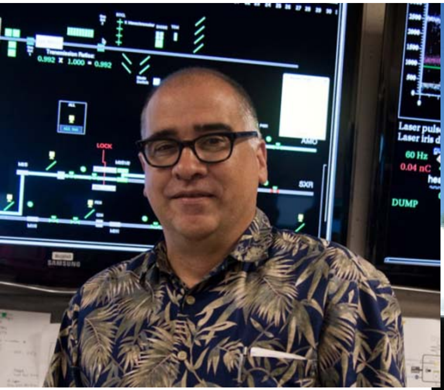
J. Ullrich, D. Rolles, A. Rudenko, S. Epp *et al. (Germany)*

Additional capability: LCLS, ASG, WMU (LAMP) Multi-Purpose Chamber



- Imaging expts and photon- particle correlation exps.
- Flexible setup, multiple injectors, spectrometers, etc.
- CAMP publication: L. Struder et al., NIM A 614, 483 (2010)

Major LAMP Players



SUMMARY

- **Sequential Cyclic Multiple Ionization is dominant mechanism with X-rays. Dissociation & ionization dynamics of molecules leads to *Fully Stripped* atomic fragment ion.**

- **Pulse duration dependence of the multiple ionization reveals transparency/frustrated absorption that suppresses high charge states at short pulse duration. *Impacts Positively Single Pulse Imaging Applications*.**

- **Double Core Vacancies beat the Auger clock. Characterization of DCH states in molecules for ESCA.**

- **Future Collaboration (US, SW, IT, JP,GE) Beamtime Spring 2012.**

Collaboration (‘10) II, CO..

Collaboration I ('09): N_2, H_2S, SF_6