

# Light-induced ultrafast structural rearrangements in the hybrid perovskites

Aaron M. Lindenberg

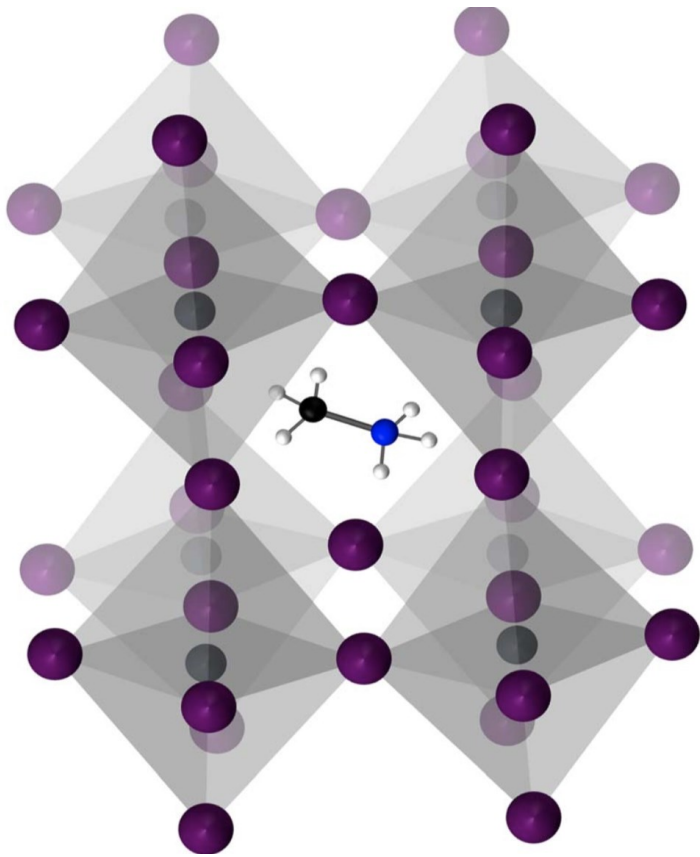
Department of Materials Science and Engineering, Stanford University  
SLAC National Accelerator Laboratory

- Outline:
1. THz emission studies
  2. Femtosecond electron diffraction results
  3. First measurements at XFEL.

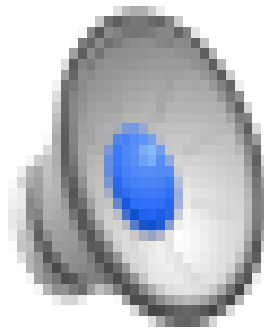
European XFEL User's Meeting  
Hamburg, Germany  
January 24, 2017

# Dynamics plays a central role in the functionality of materials and devices

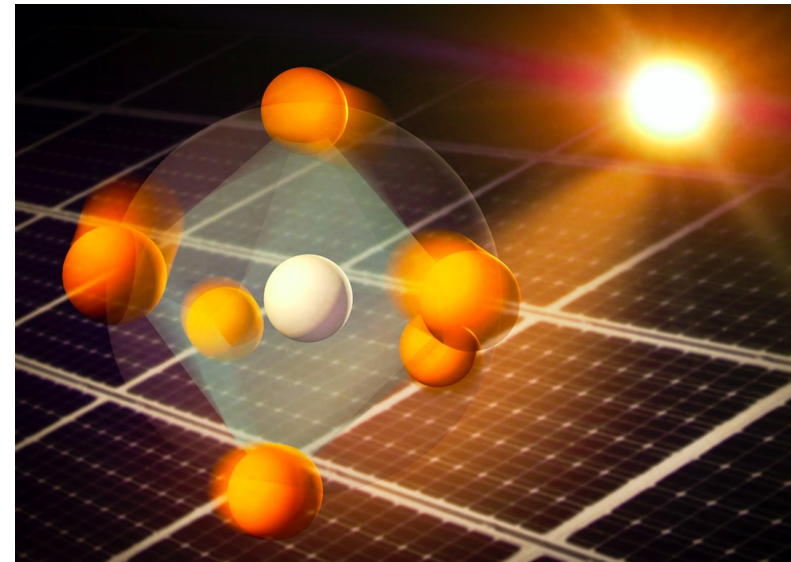
Materials for photovoltaic/optoelectronic applications



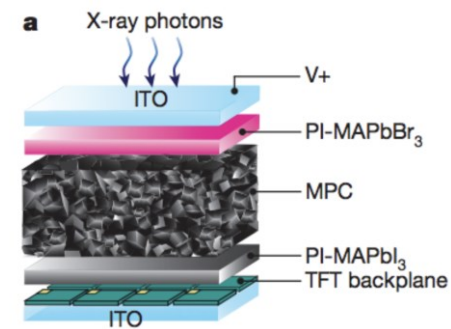
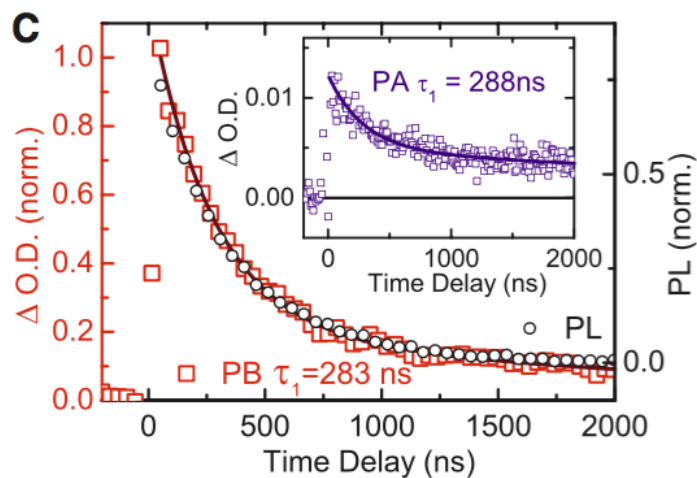
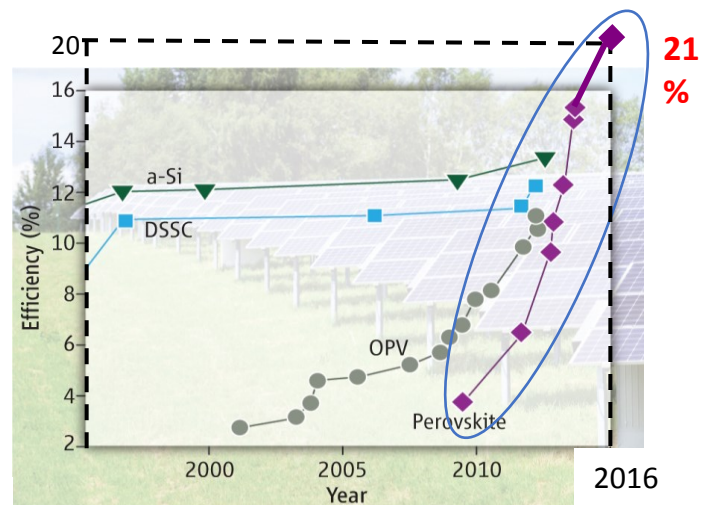
Miyata et al., Sci. Adv. (2017)



Aron Walsh et al.



# What are the structural origins of optoelectronic functionality (and degradation) in the hybrid perovskites?



LETTER

doi:10.1038/nature24032

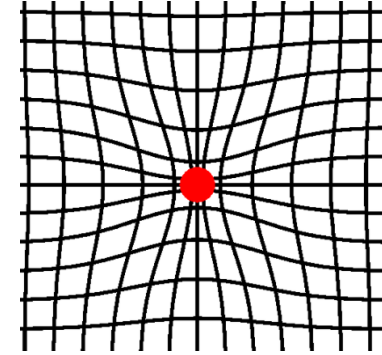
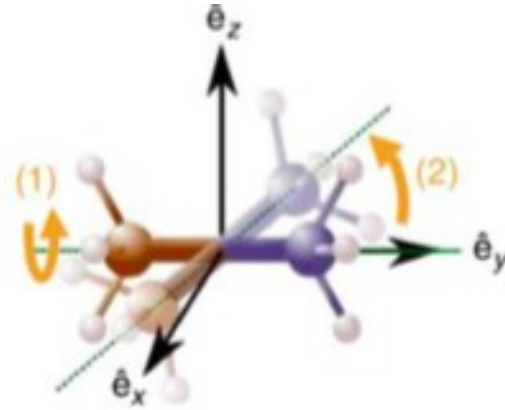
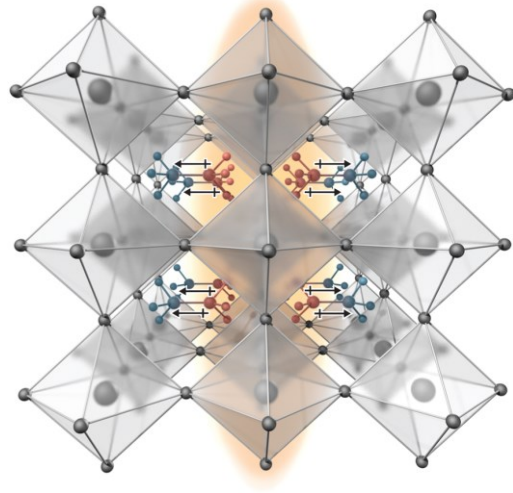
## Electron-Hole Diffusion Lengths Exceeding 1 Micrometer in an Organometal Trihalide Perovskite Absorber

Samuel D. Stranks,<sup>1</sup> Giles E. Eperon,<sup>1</sup> Giulia Grancini,<sup>2</sup> Christopher Menelaou,<sup>1</sup> Marcelo J. P. Alcocer,<sup>2</sup> Tomas Leijtens,<sup>1</sup> Laura M. Herz,<sup>1</sup> Annamaria Petrozza,<sup>2</sup> Henry J. Snaith<sup>1\*</sup>

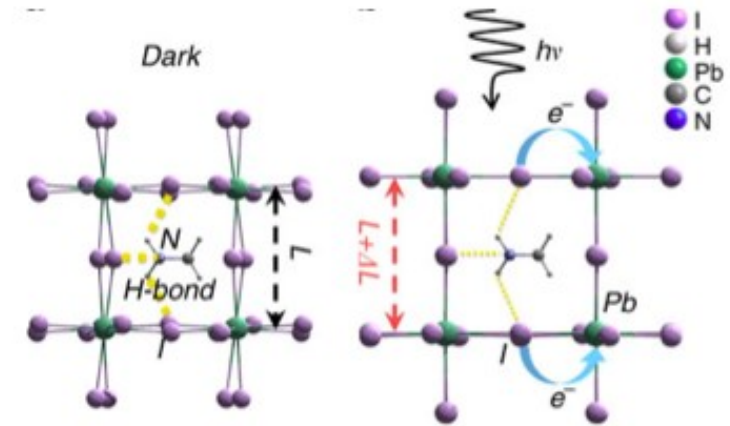
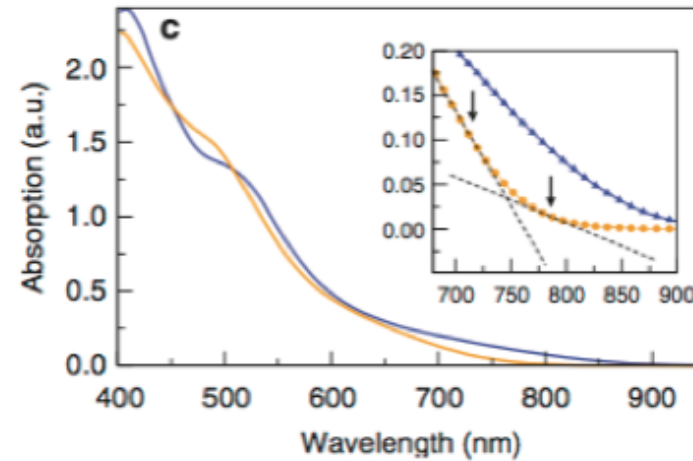
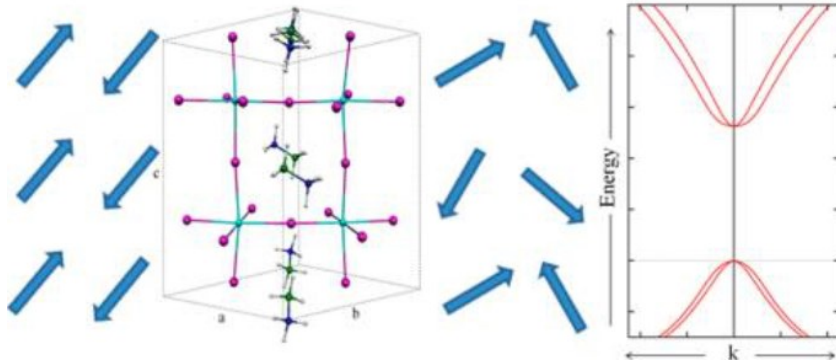
## Printable organometallic perovskite enables large-area, low-dose X-ray imaging

Yong Churl Kim<sup>1</sup>, Kwang Hee Kim<sup>1</sup>, Dae-Yong Son<sup>2</sup>, Dong-Nyuk Jeong<sup>2</sup>, Ja-Young Seo<sup>2</sup>, Yeong Suk Choi<sup>1</sup>, In Taek Han<sup>1</sup>, Sang Yoon Lee<sup>1</sup> & Nam-Gyu Park<sup>2</sup>

# Coupling between optoelectronic properties and ultrafast structural dynamics

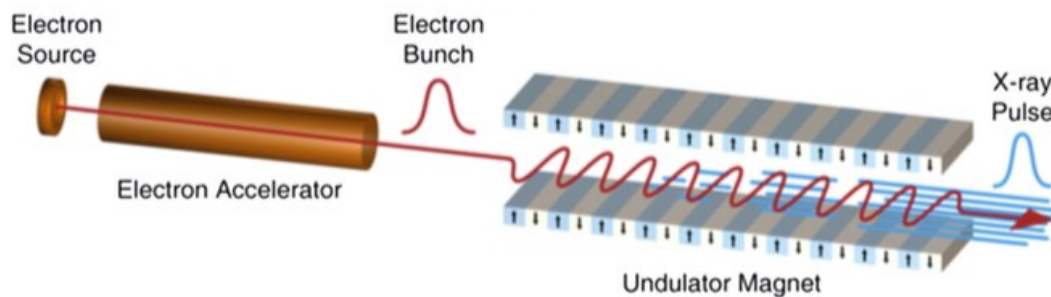


Centrosymmetric structure  $\rightarrow$  Dynamics  $\rightarrow$  Rashba splitting

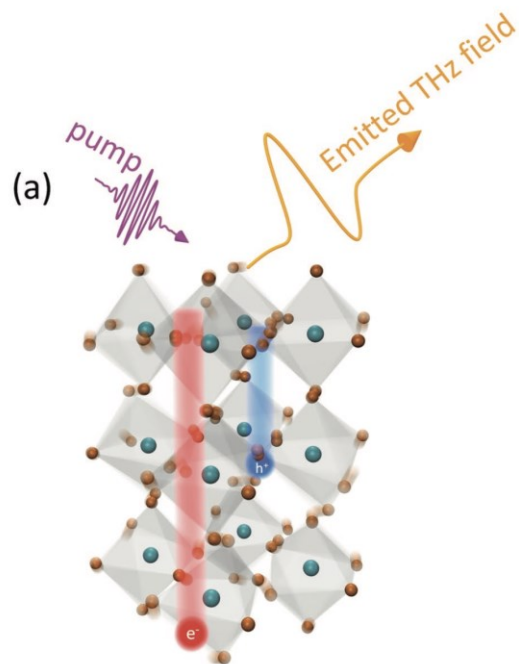


- Motta et al. Nat. Commun. 6, 7026 (2015)
- Zhou et al., Nat. Commun. 7, 11193 (2016)
- T. Etienne et al. JPCL (2016)
- Zhu et al., Science, 353, 1409 (2016)
- Leppert et al., JPCL (2016)

# THz emission as a probe of time-dependent currents and associated unit cell deformations

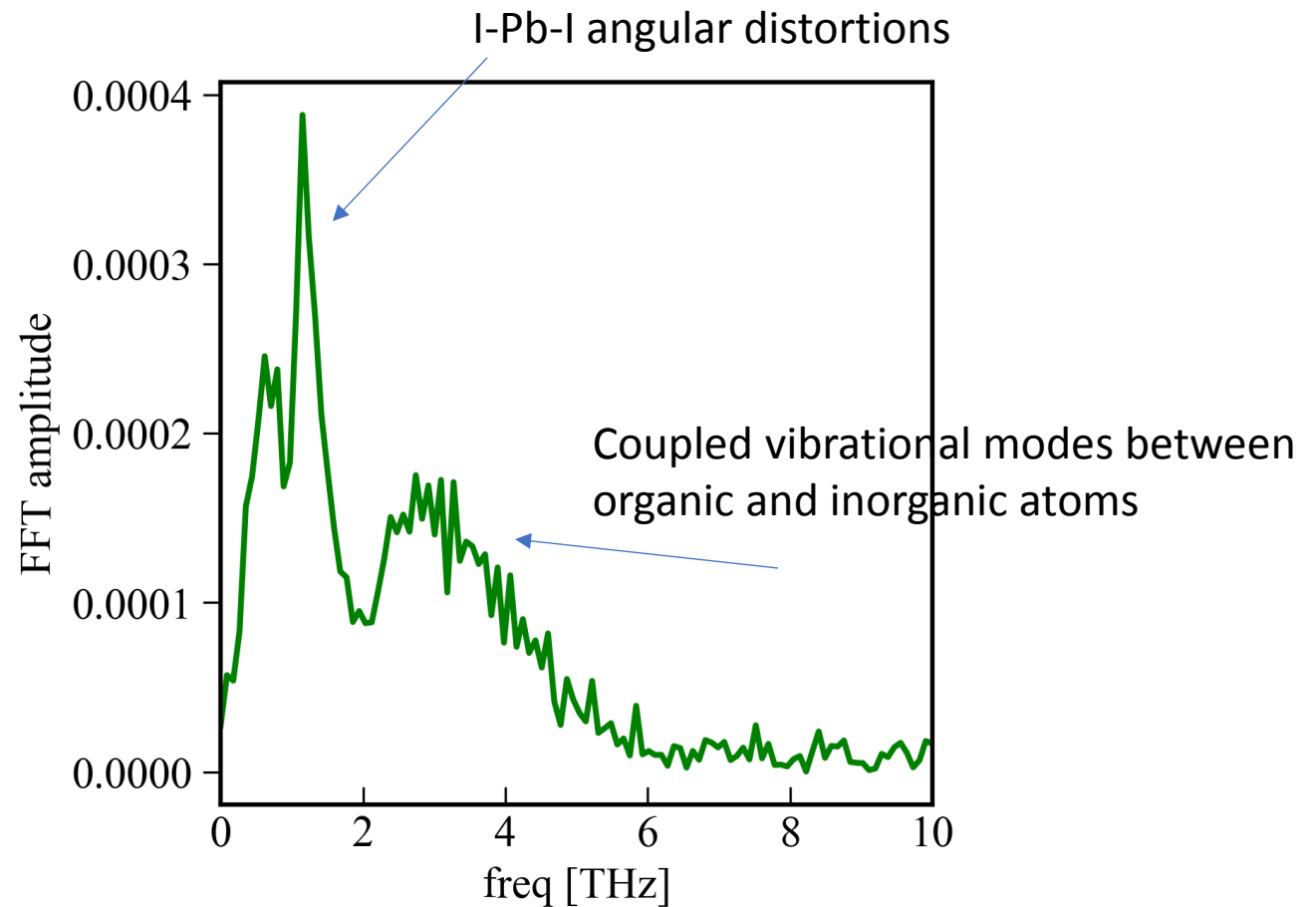
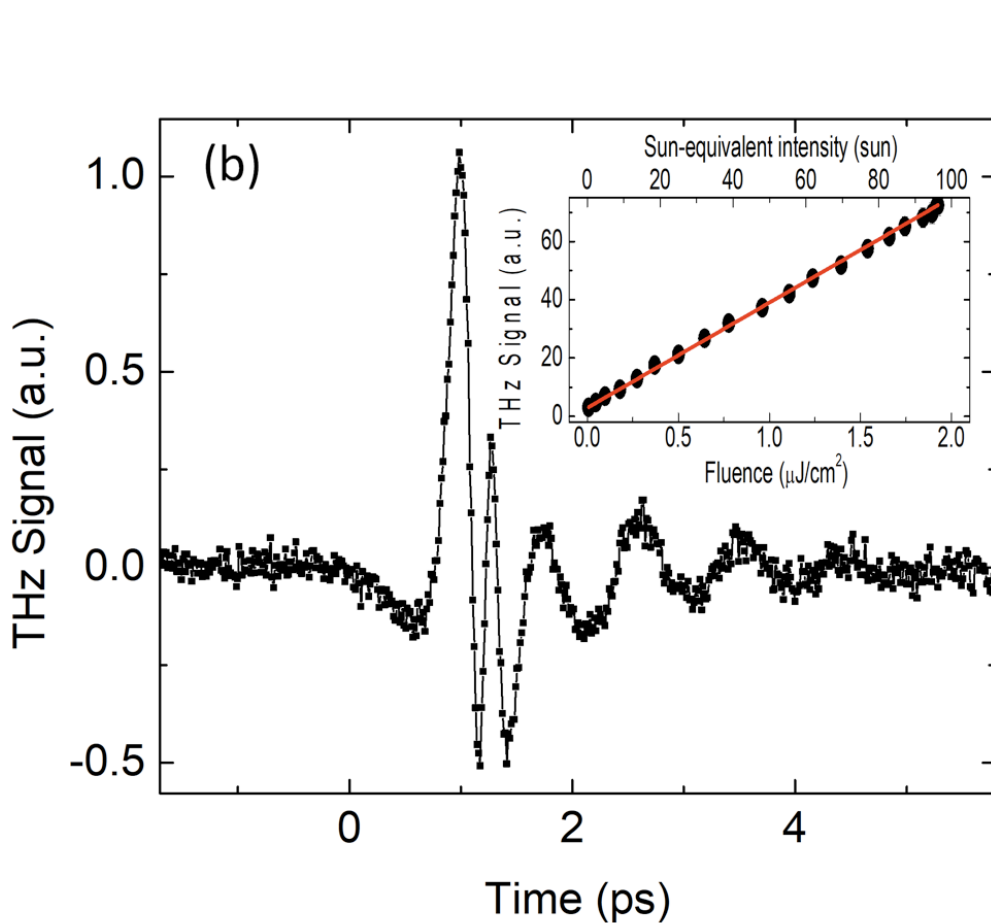


Pellegrini et al., RMP (2016)



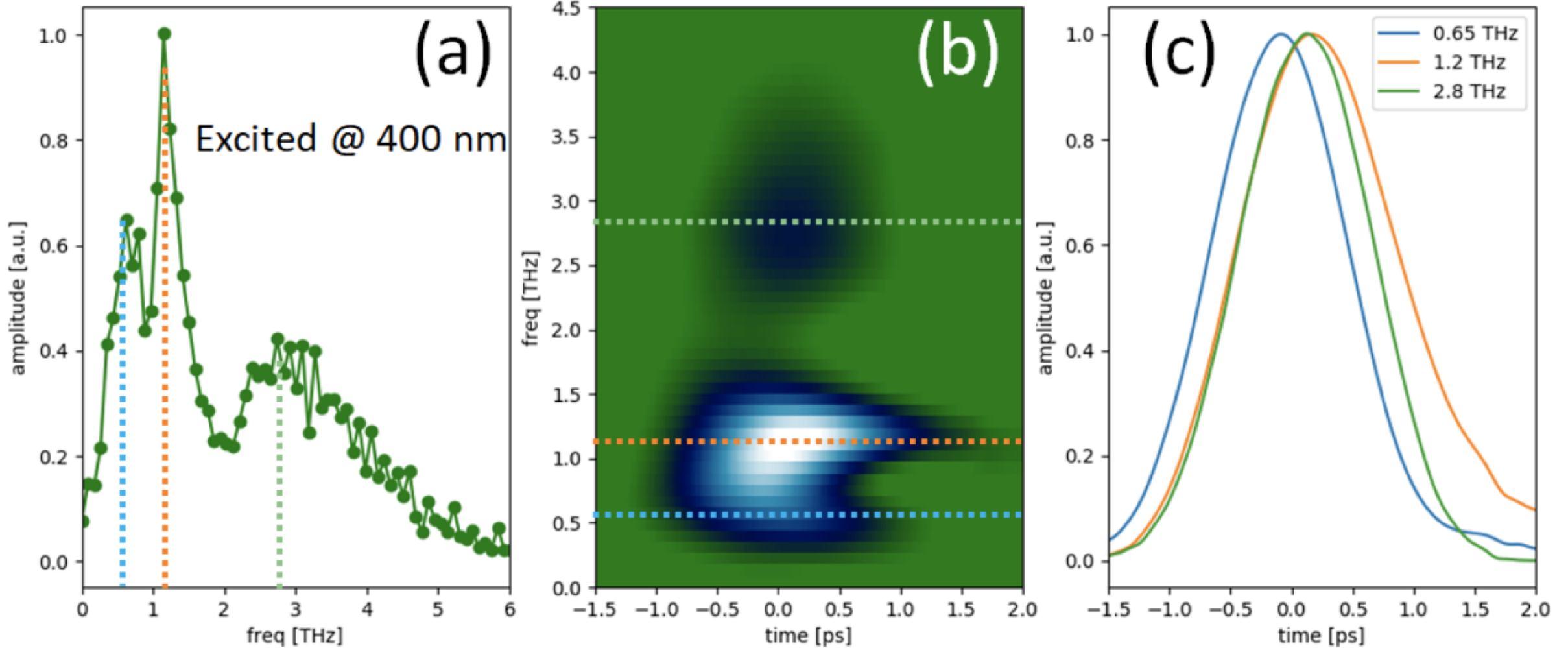
$$E_{\text{THz}}(t) \propto \frac{\partial J(t)}{\partial t}$$

# Terahertz emission from the hybrid perovskites (MAPbI<sub>3</sub>)

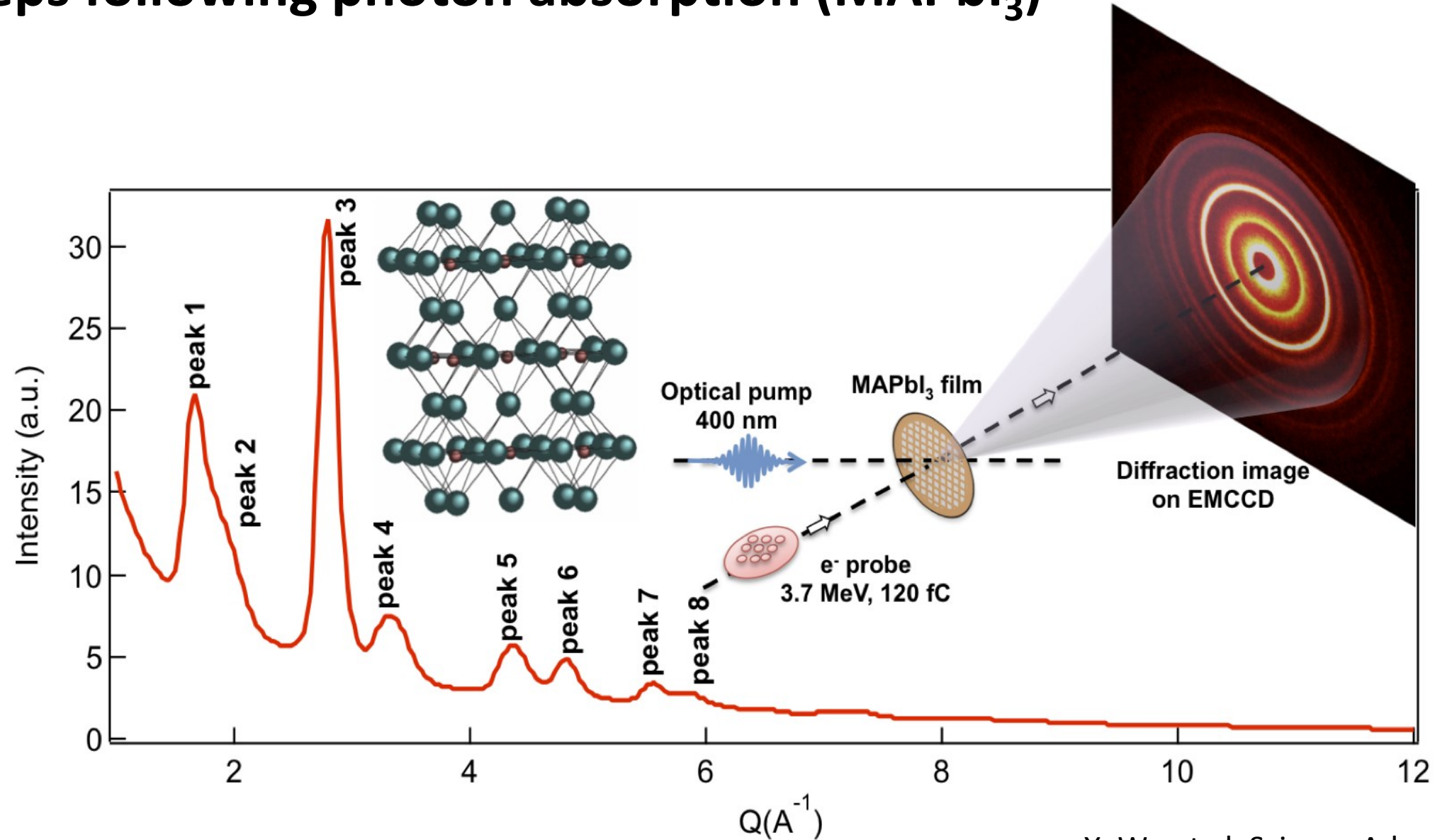


**Indicates ultrafast charge separation and associated strong electron-phonon coupling processes**

# Carrier-lattice coupling via THz emission spectroscopy



# Femtosecond electron scattering measurements of first steps following photon absorption (MAPbI<sub>3</sub>)

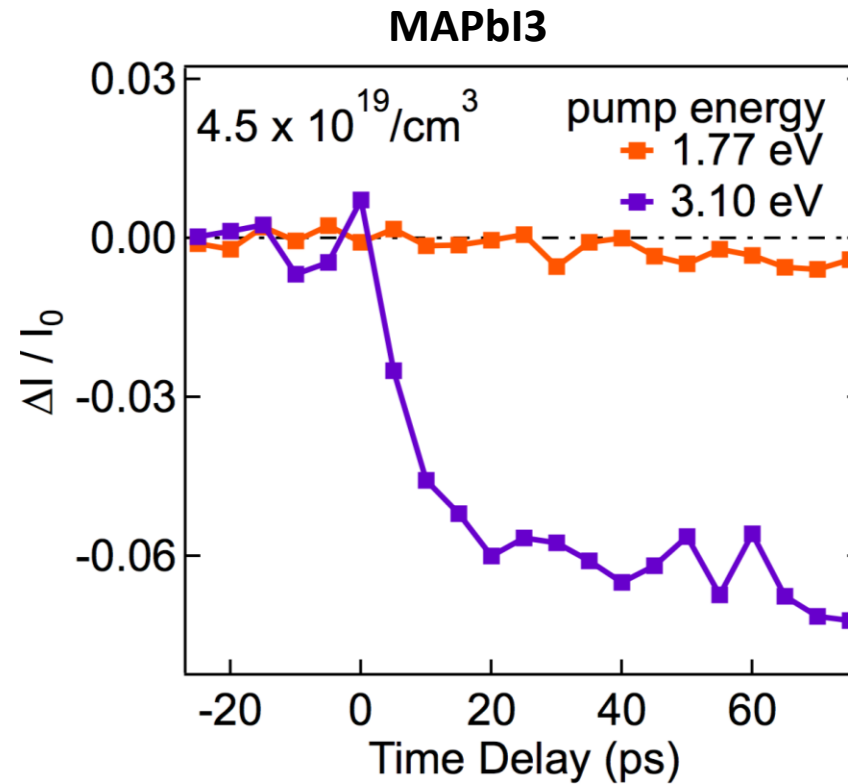
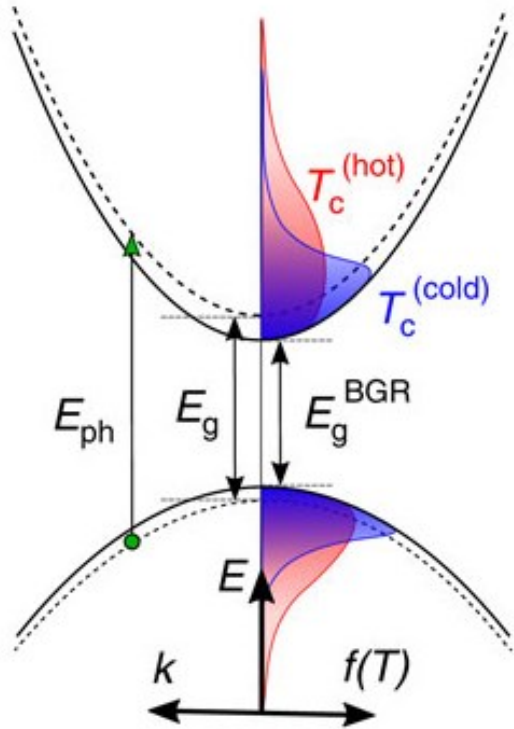




# Hot carrier – lattice interactions

$$F = \sum_n f_n e^{i\mathbf{Q} \cdot \mathbf{r}_n}$$

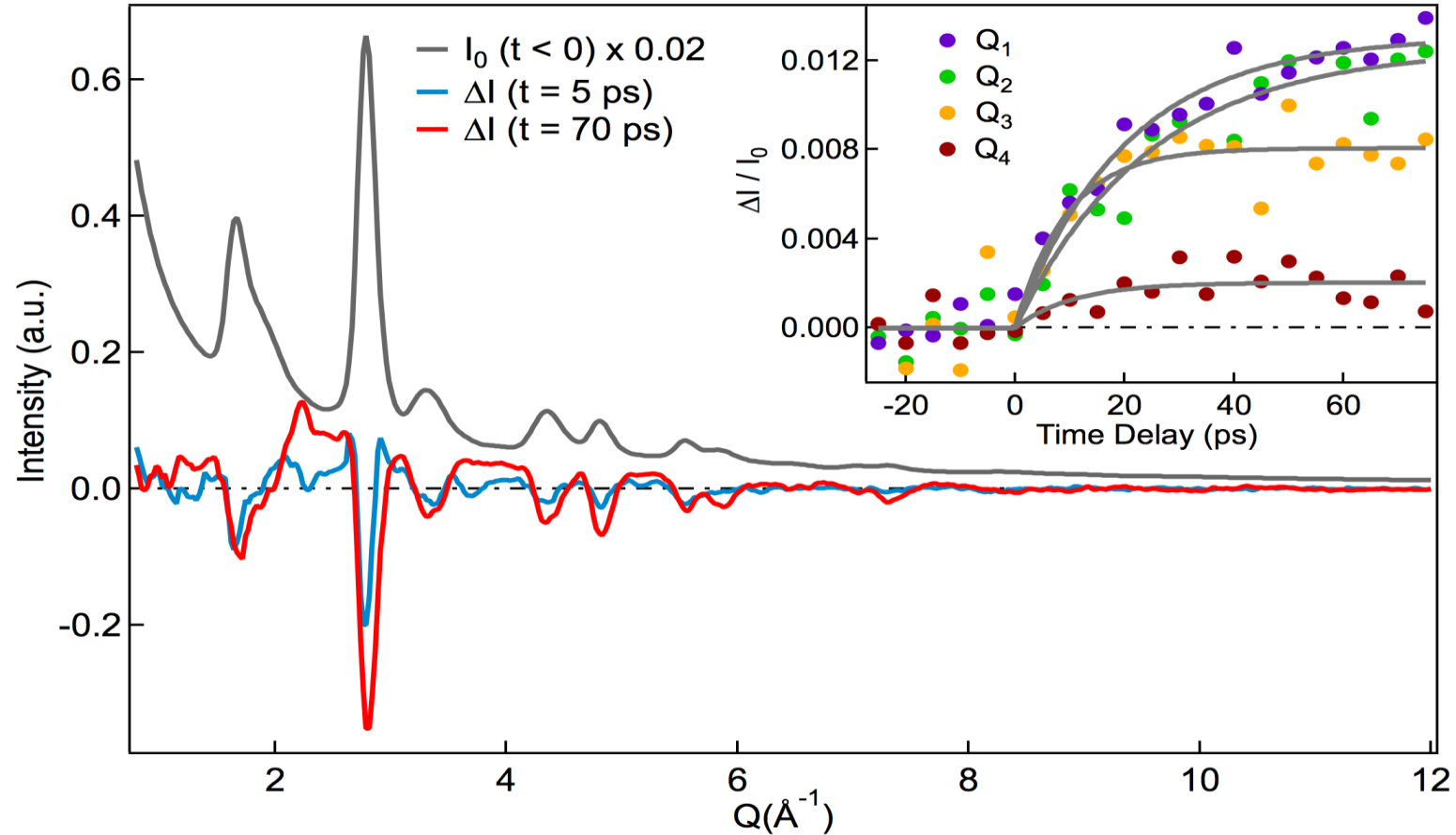
$$I(Q) = I_0 e^{-\frac{Q^2 \langle u^2(t) \rangle}{3}}$$



E. Mannebach et al., Nano Lett. (2015)

X. Wu et al., Sci. Adv. (2017)

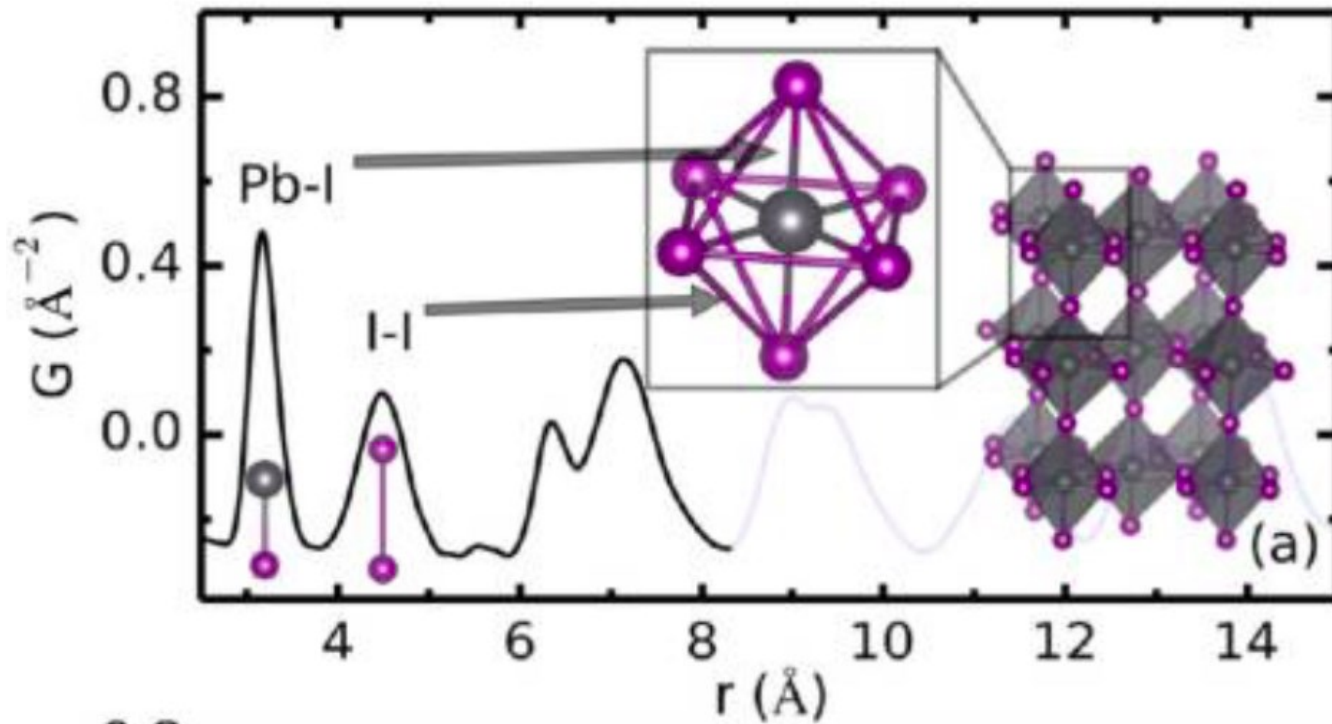
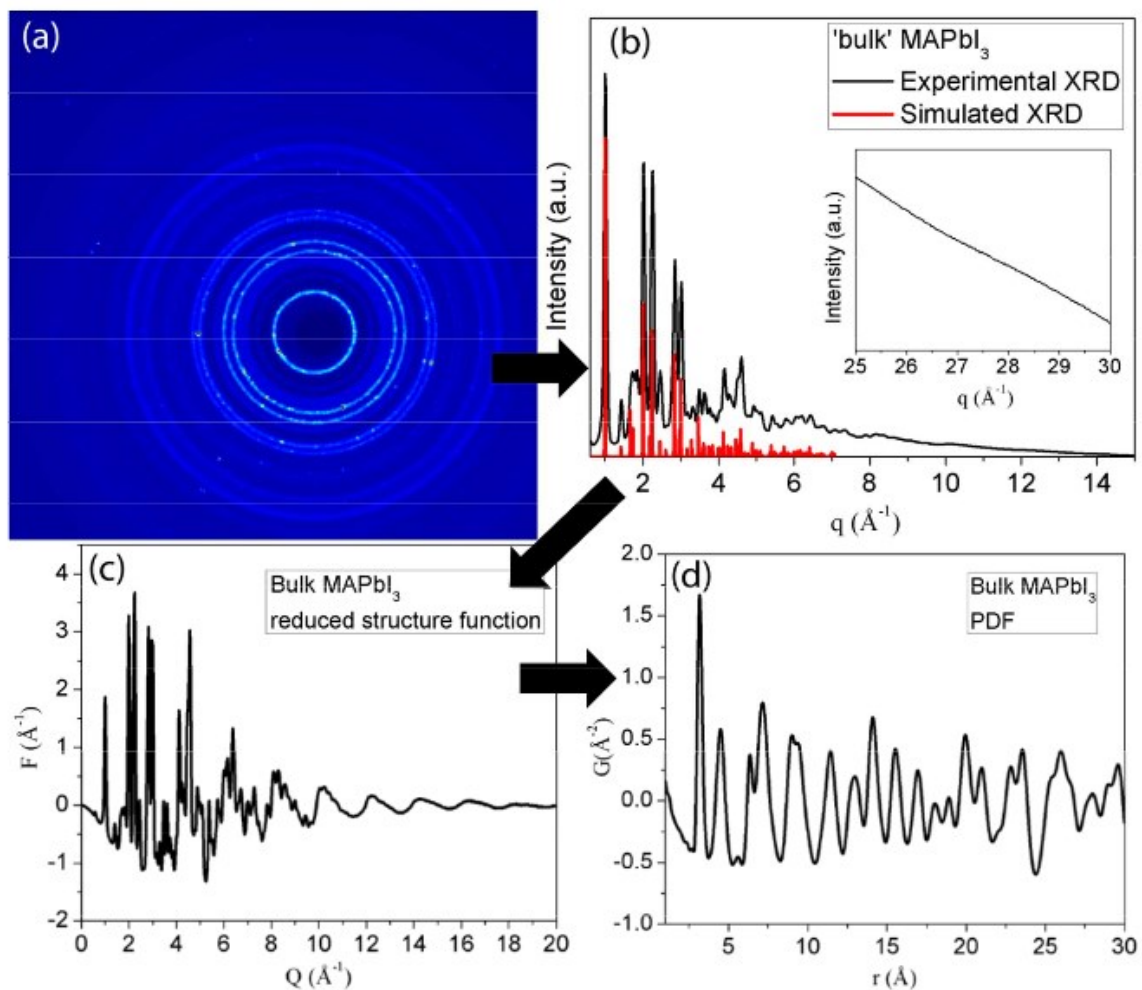
# Pair distribution function analysis



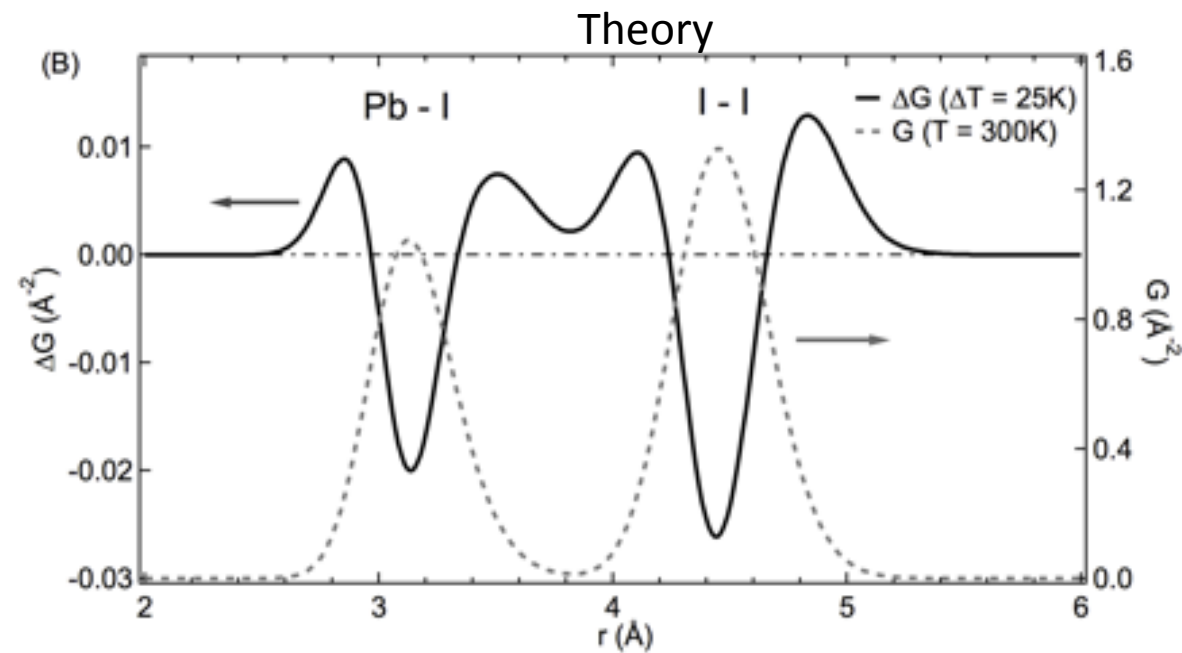
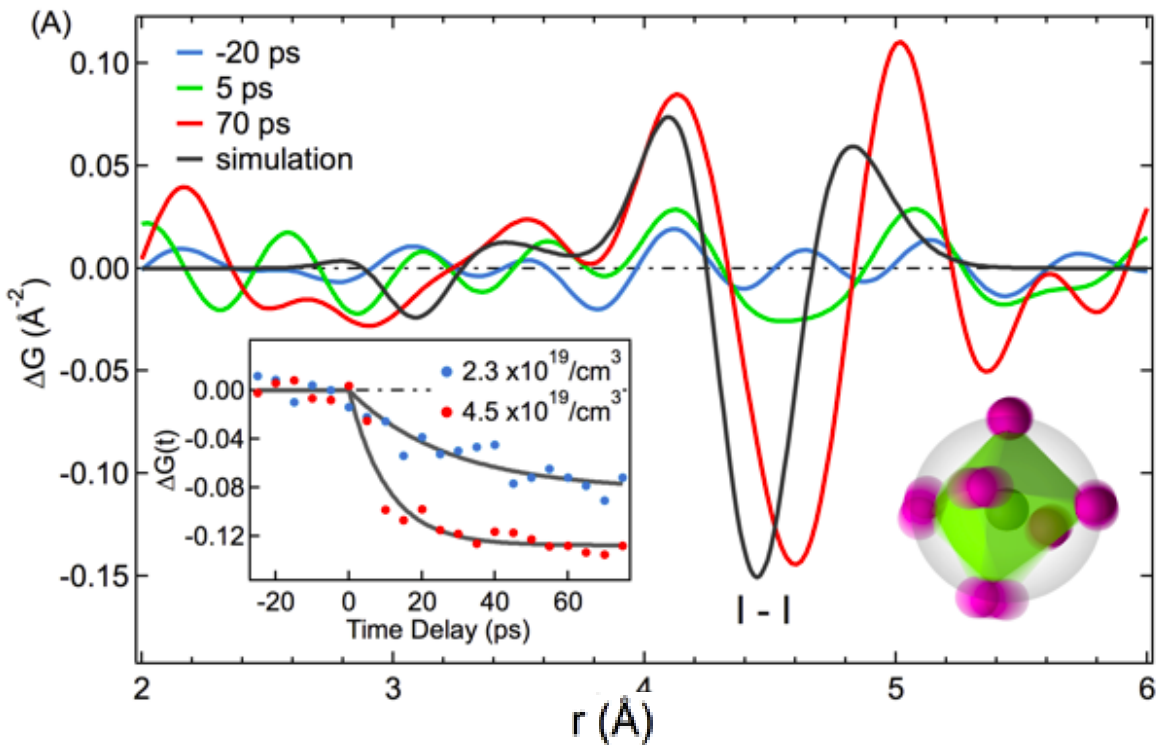
$$\Delta G(r, t) = \int_0^{\infty} Q \Delta S(Q, t) \sin(Qr) dQ$$

-Gives interatomic distance distribution e.g. probability of finding atomic pairs a distance  $r$  apart

# Static pair distribution function: MAPbI<sub>3</sub>



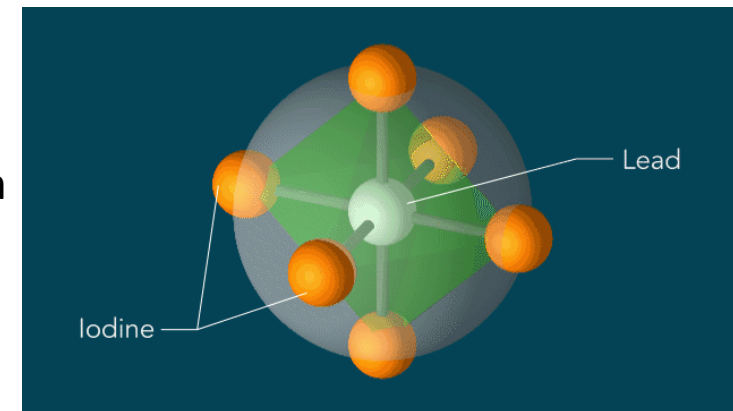
# Time-resolved PDF: Dominant response at I-I correlation peak.



-Large amplitude changes observed in the differential pair correlation function at the I-I distance. Broadening by an amount comparable to its intrinsic width under photo-induced temperature jumps of  $\sim 10$  K. Effect much larger than predicted for simple T-jump and much more anisotropic.

-No change at the Pb-I distance.

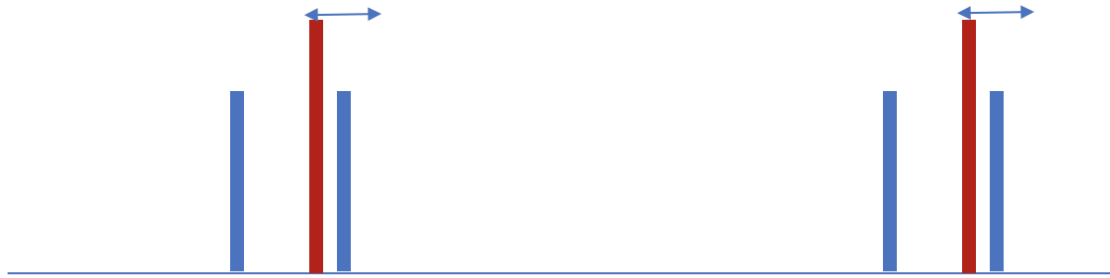
-Indicative of a rotationally-disordered octahedral structure; volume-preserving distortions of  $I_6$  cages.



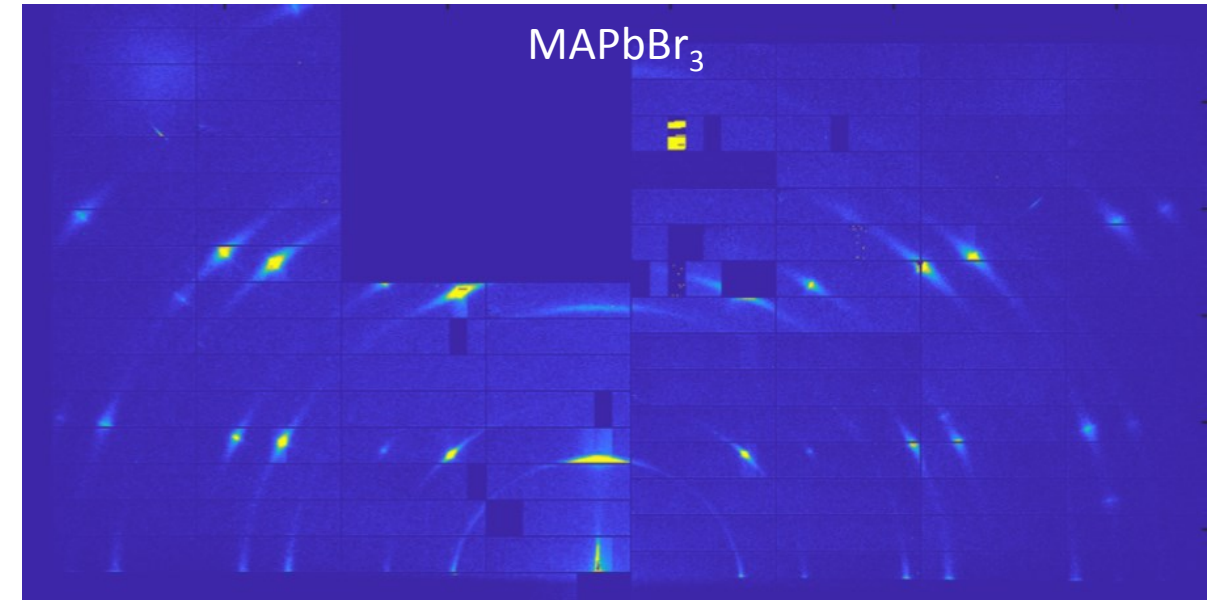
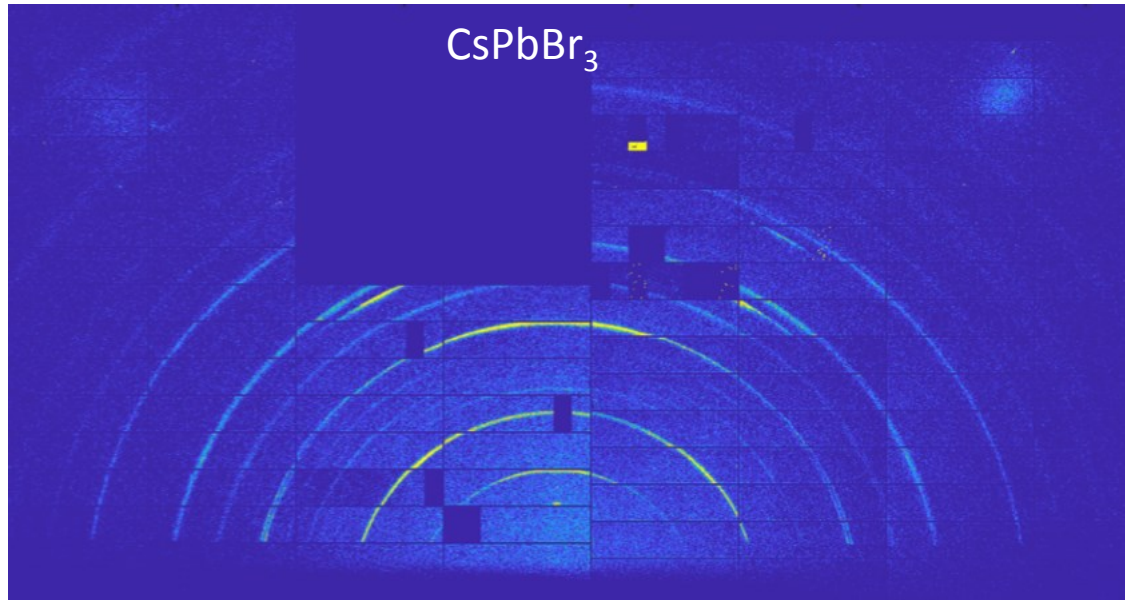
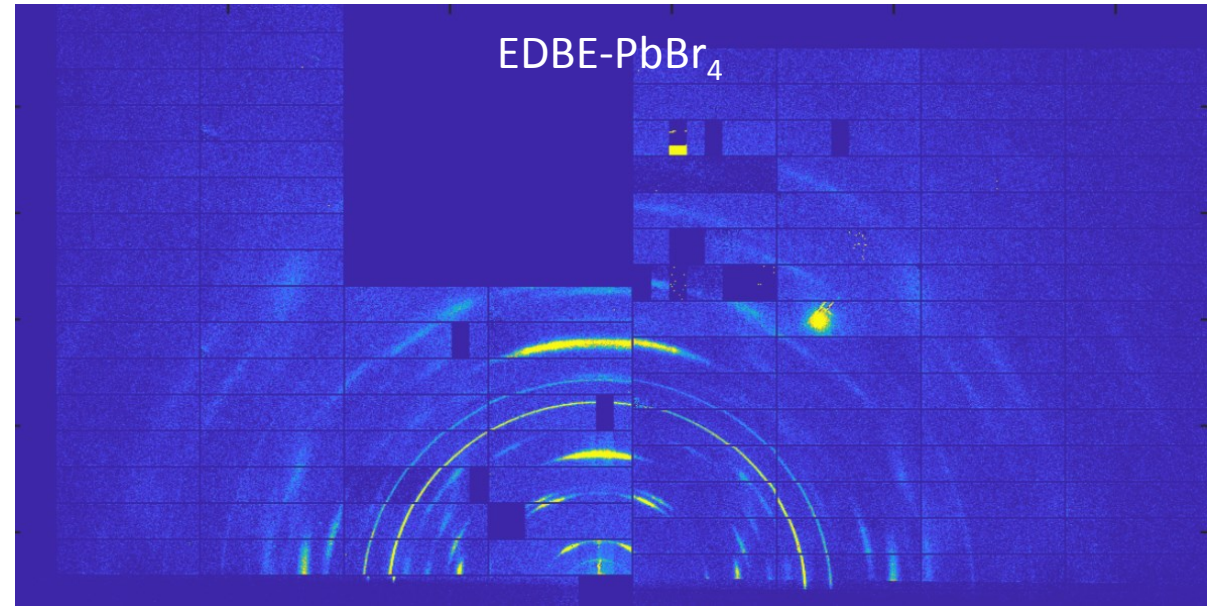
## FXE measurements (September, 2017)

Bunch pattern:

(2 x-ray bunches/burst as probe and reference)

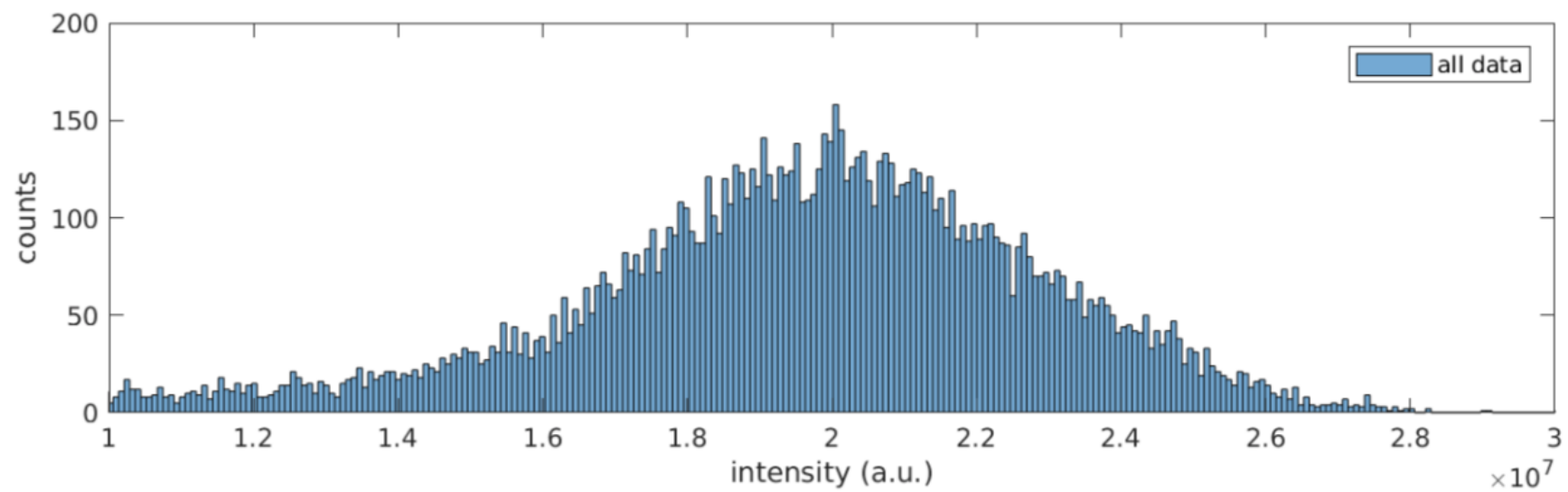
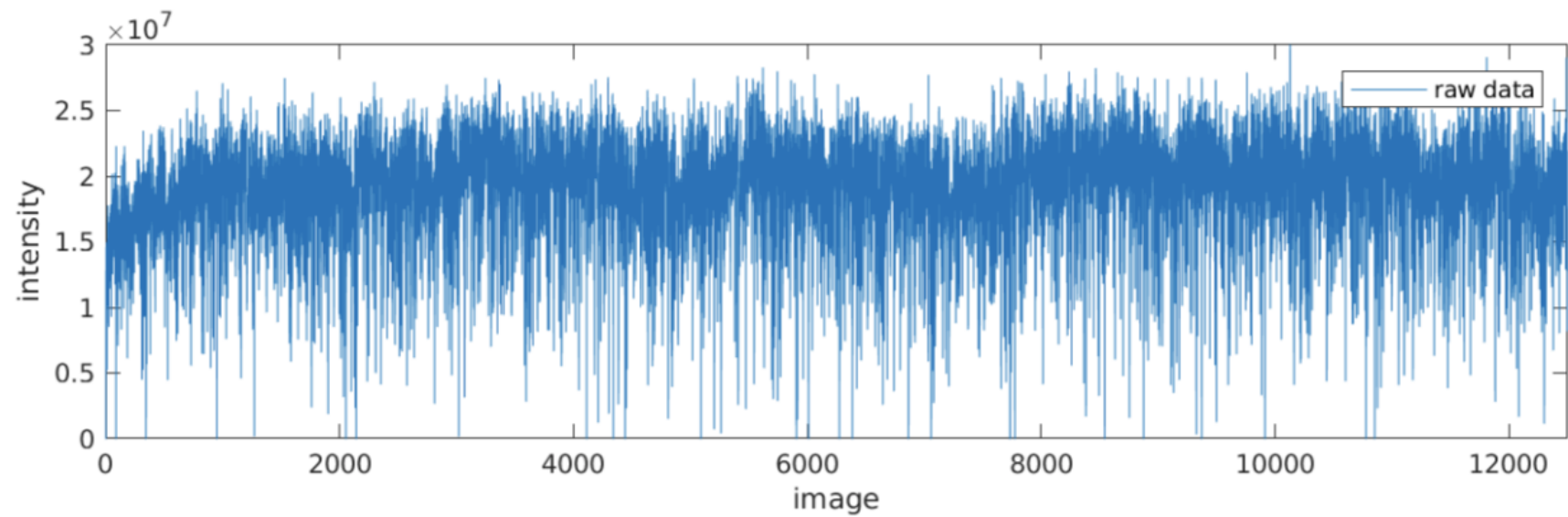


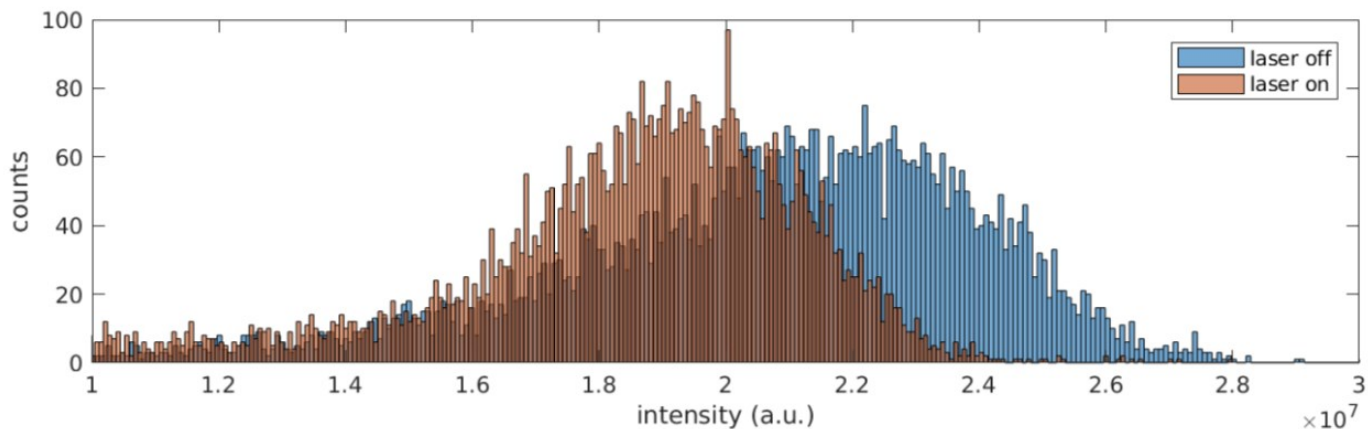
Excitation with fiber laser oscillator only (pump fluence  $\sim 1 \mu\text{J}/\text{cm}^2$ )



Patterns consistent with expectation. Reasonable signal even in single shot. Sample damage not a significant issue under reasonable x-ray excitation conditions.

Sample data (integration over ROI)

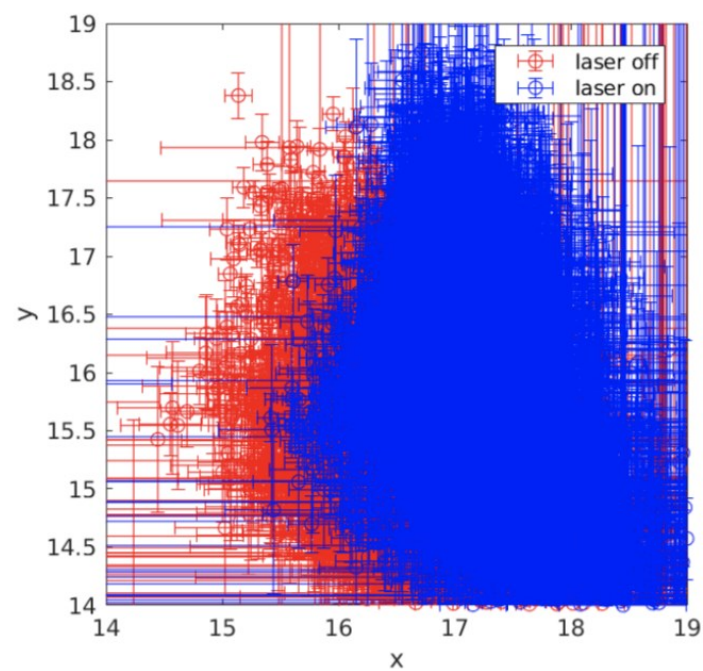
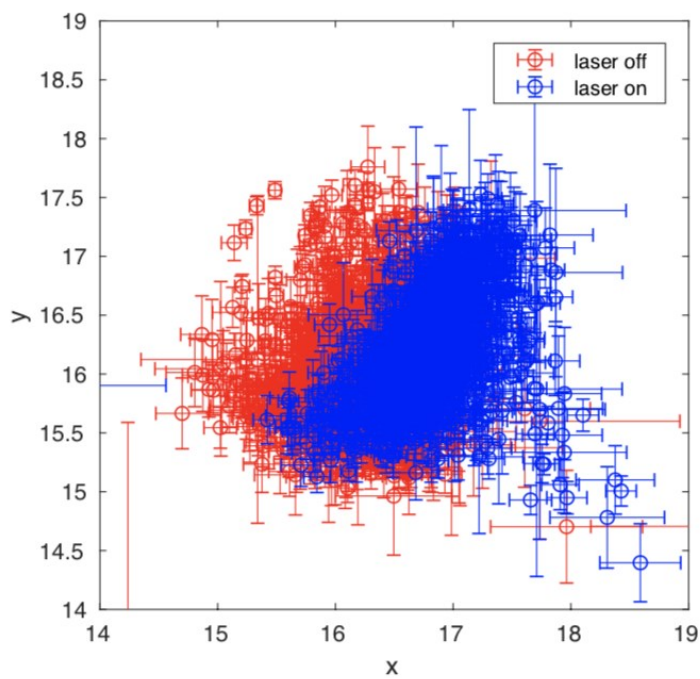
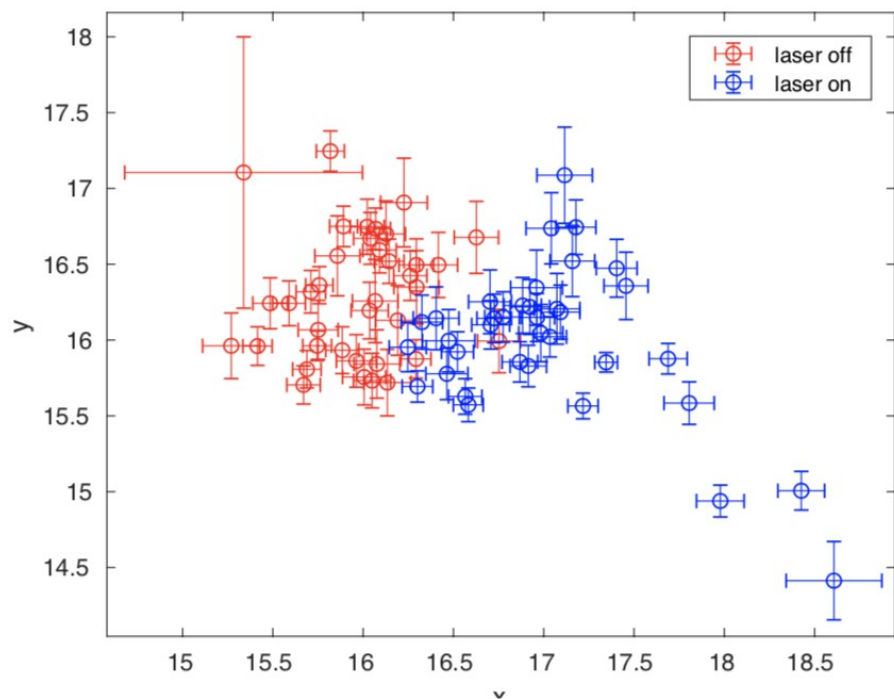




First ~50 peak positions

First ~1800 peak positions

All ~12500 peak positions

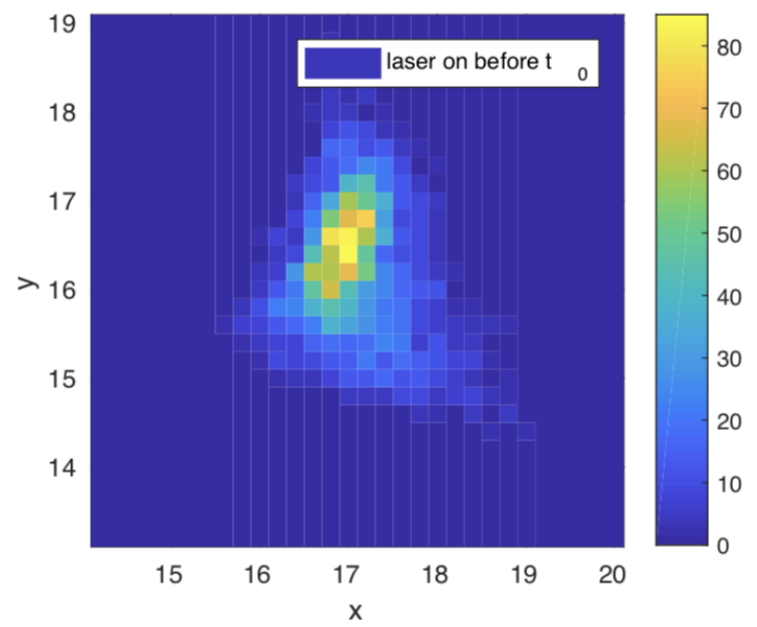
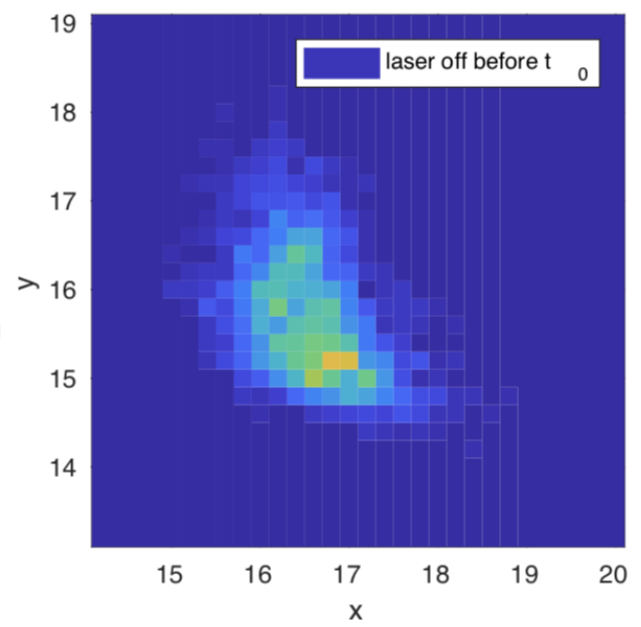


Possible x-ray-induced effects...

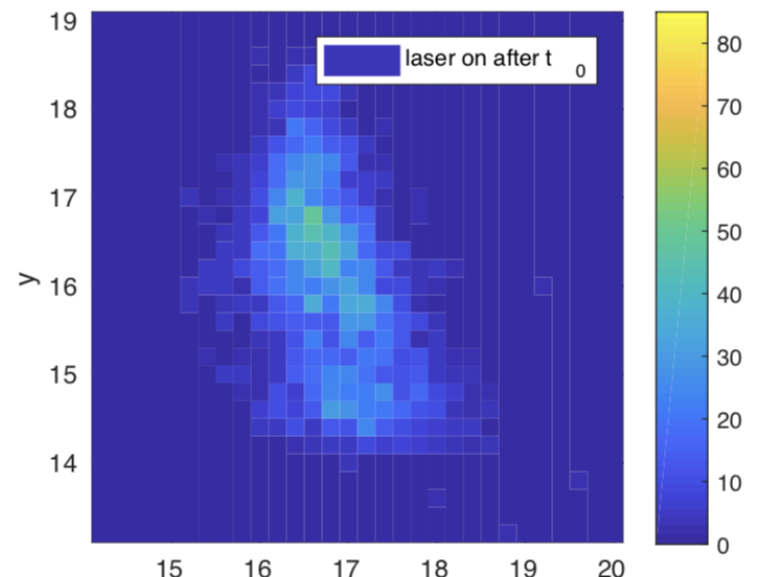
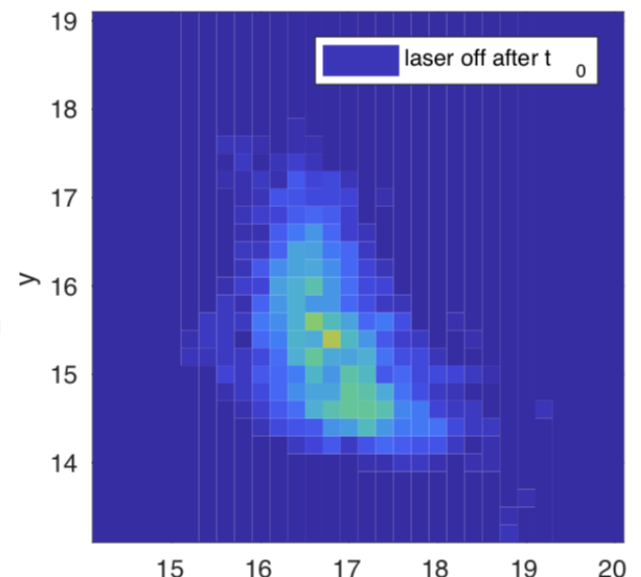
laser off ↓

laser on ↓

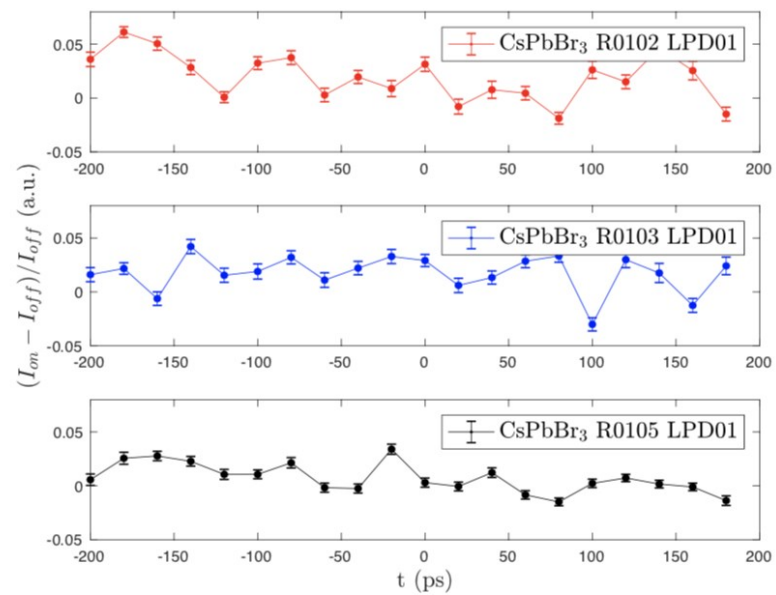
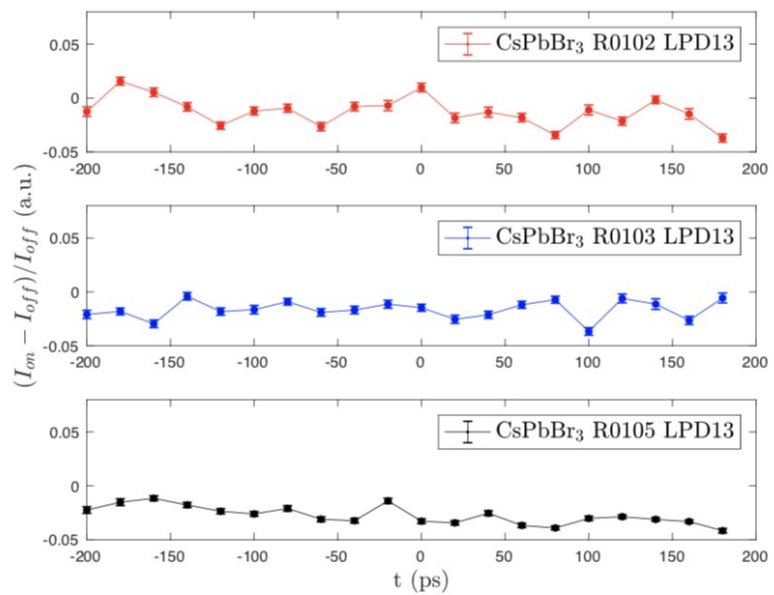
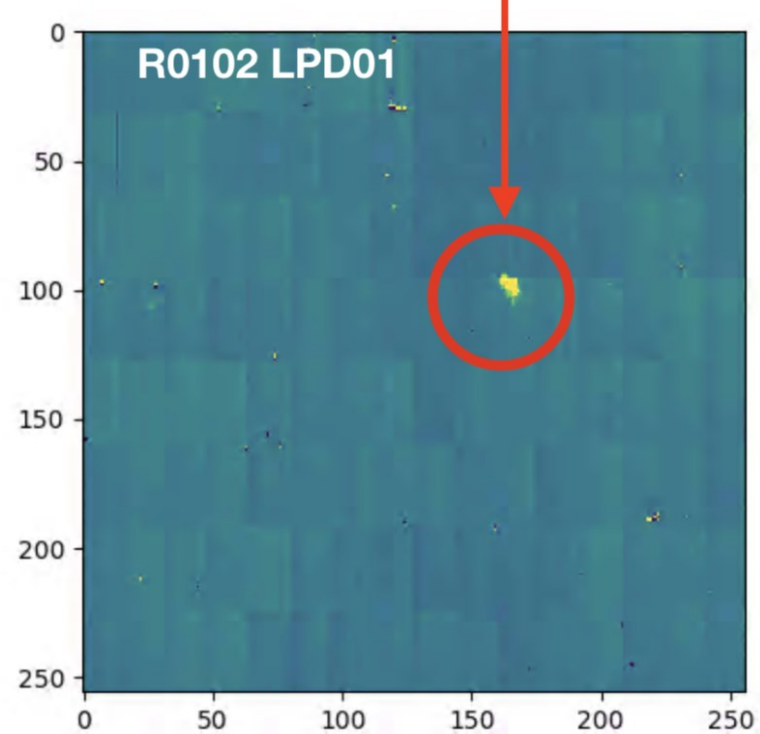
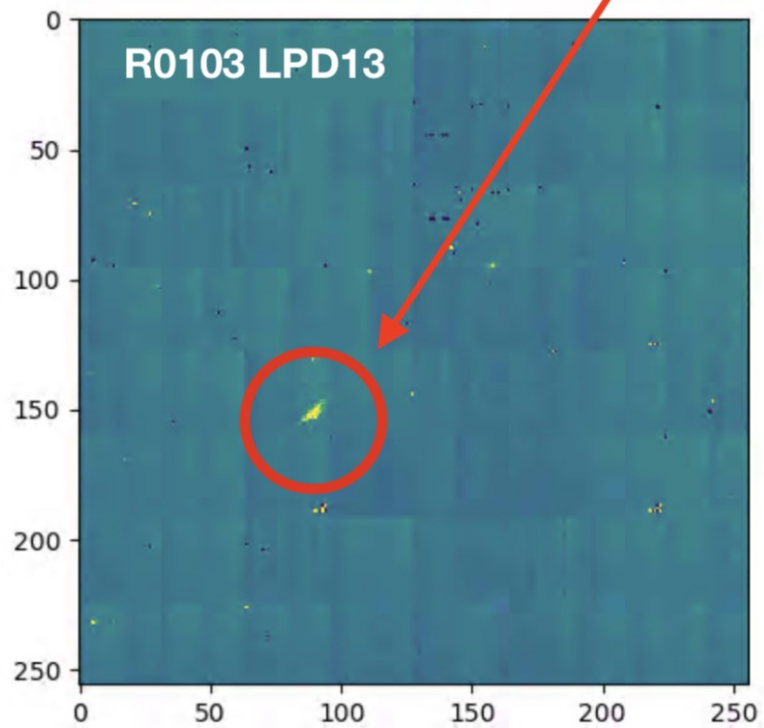
before  $t_0$   
(image < 3000)  
→



after  $t_0$   
(image > 3000)  
→







# Key takeaways from first round of measurements:

- a) In grazing incidence geometry, samples survive XFEL beam for periods of hours in a regime which allows for clean measurements of diffraction patterns.
- b) Signal to noise in scattering geometry at the 1% level achievable.
- c) Analysis ongoing. Followup beamtime scheduled in May.
- d) With ongoing improvements to FXE beamline, high sensitivity ultrafast measurements should be possible in low excitation limit.

# Acknowledgements:

**Stanford/SLAC:** Matthew Smith, Burak Guzelturk, Mariano Trigo, Sam Teitelbaum, Edbert Sie, Yu Lin, Hema Karunadasa

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