Multiwavelength anomalous diffraction at high x-ray intensity

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Center for Free-Electron Laser Science
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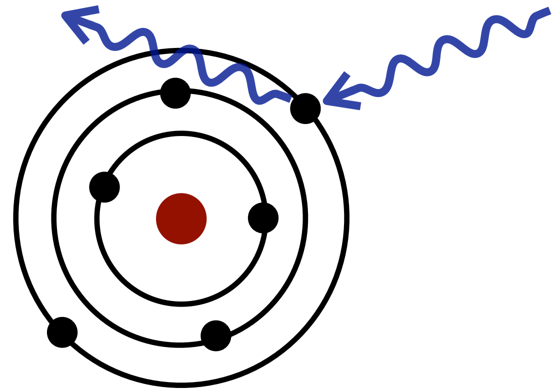
DESY – Max Planck Society – University of Hamburg

X-ray scattering

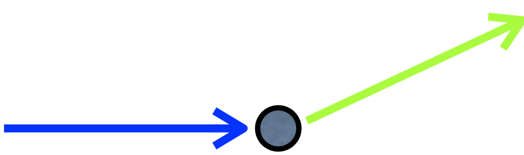
- Elastic x-ray scattering form factor

$$f^0(\mathbf{Q}) = \int d^3r\ \rho(\mathbf{r})\ e^{i\mathbf{Q}\cdot\mathbf{r}}$$

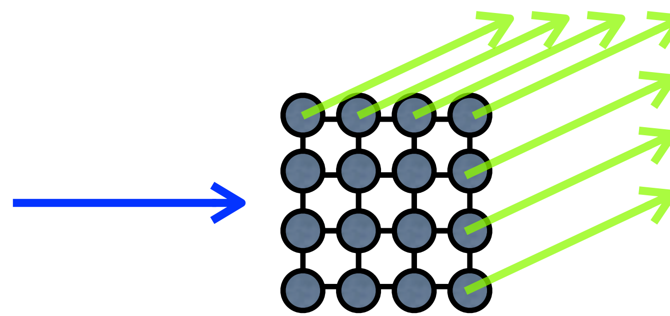
$$\frac{d\sigma(\mathbf{Q})}{d\Omega} = \left(\frac{d\sigma}{d\Omega}\right)_T \left|f^0(\mathbf{Q})\right|^2$$



- Carbon at synchrotron radiation: 12 keV, 10^6 photons on 10μm × 10μm

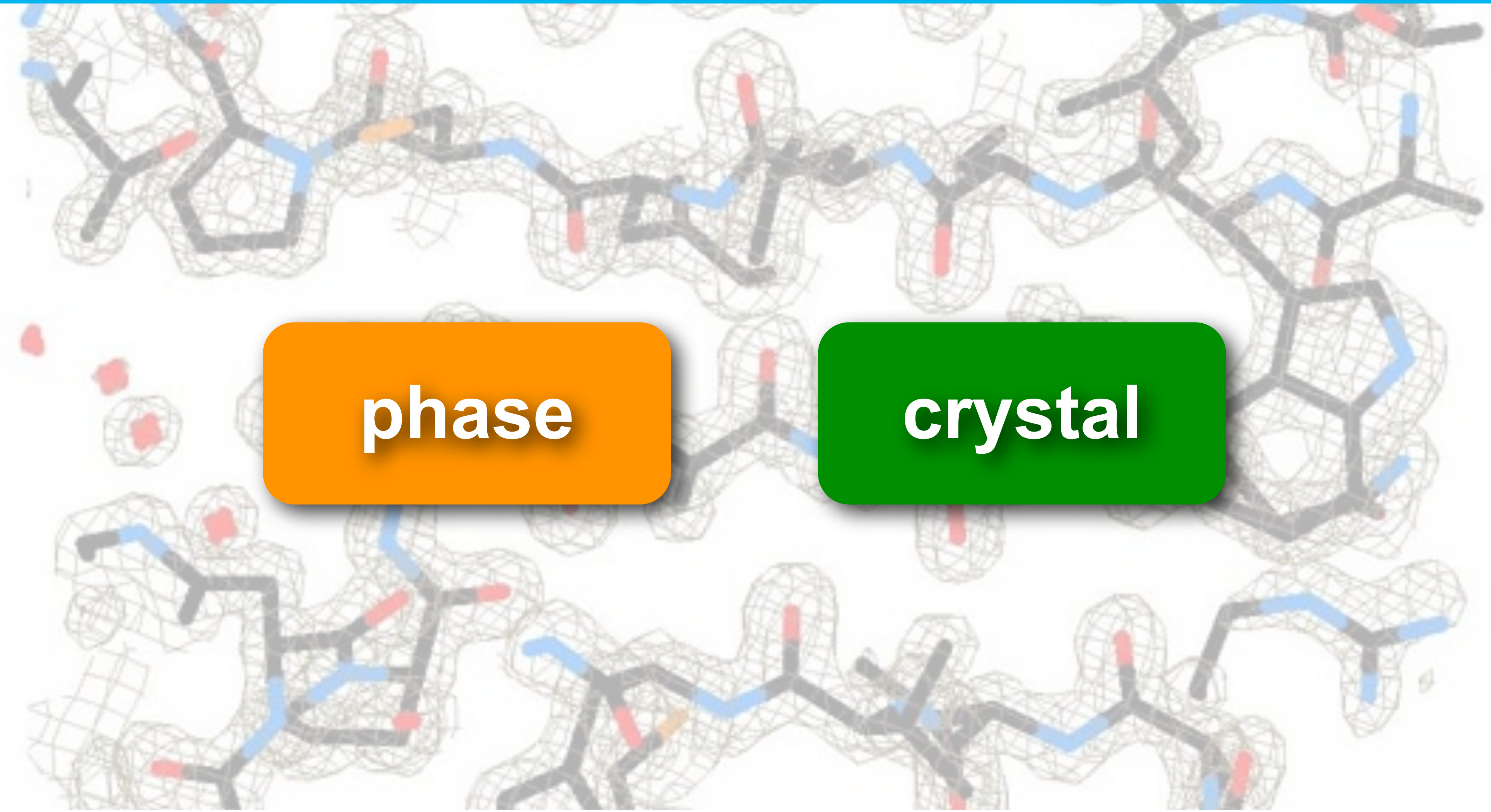


scattering
probability ~ 10^{-12}



~10^8 molecules in a crystal:
diffraction patterns
→ **X-ray crystallography**

Bottlenecks in X-ray crystallography



phase

crystal

Figure taken from http://www.jic.ac.uk/staff/david-lawson/xtallog/summary.htm

Phase problem

- Phase problem: a fundamental obstacle in constructing an electronic density map from x-ray diffraction

$$f^0(\mathbf{Q}) = \int d^3r\ \rho(\mathbf{r})\ e^{i\mathbf{Q}\cdot\mathbf{r}} = |f^0(\mathbf{Q})|\ e^{i\phi^0(\mathbf{Q})}$$

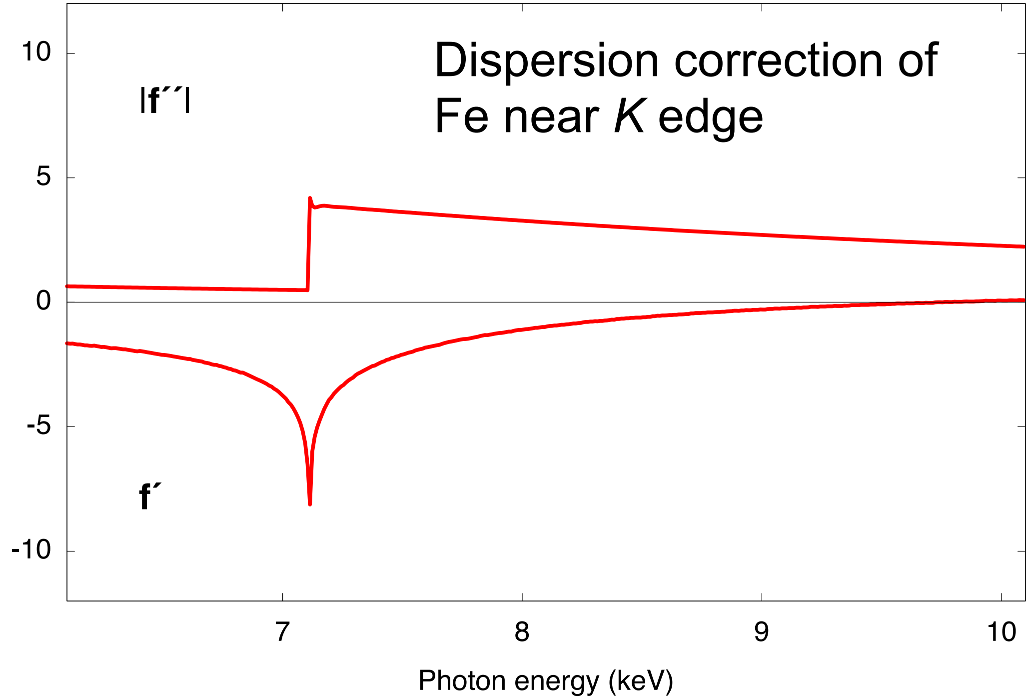
- Phases are essential for structural determination, but they are lost in measurement.
- Phasing method: how to recover phases
- MAD (Multiwavelength Anomalous Diffraction) is one of the most powerful phasing methods.

Multiwavelength Anomalous Diffraction

> Dispersion correction: $f(\mathbf{Q},\omega) = f^0(\mathbf{Q}) + f'(\omega) + if''(\omega)$

> MAD phasing:
The Karle-Hendrickson equation provides a simple way for phasing from the contrast at two or more wavelengths.

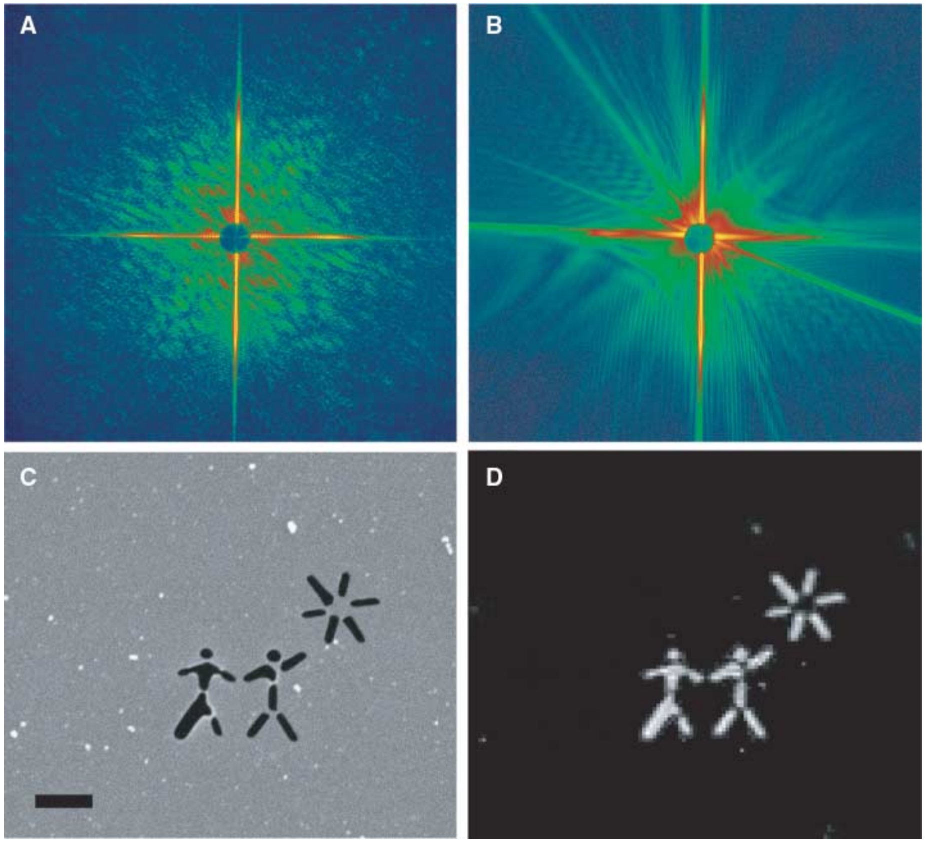
Karle, *Int. J. Quant. Chem.* **18**, Suppl. S7, 357 (1980).
Hendrickson, *Trans. Am. Crystalgr. Assoc.* **21**, 11 (1985).



> The MAD method has been a well-established phasing method with synchrotron radiation sources since late 80's: *Science* **241**, 806 (1998); *PNAS* **86**, 2190 (1989); *Science* **249**, 1398 (1990); *Science* **254**, 51 (1991).

X-ray free-electron laser

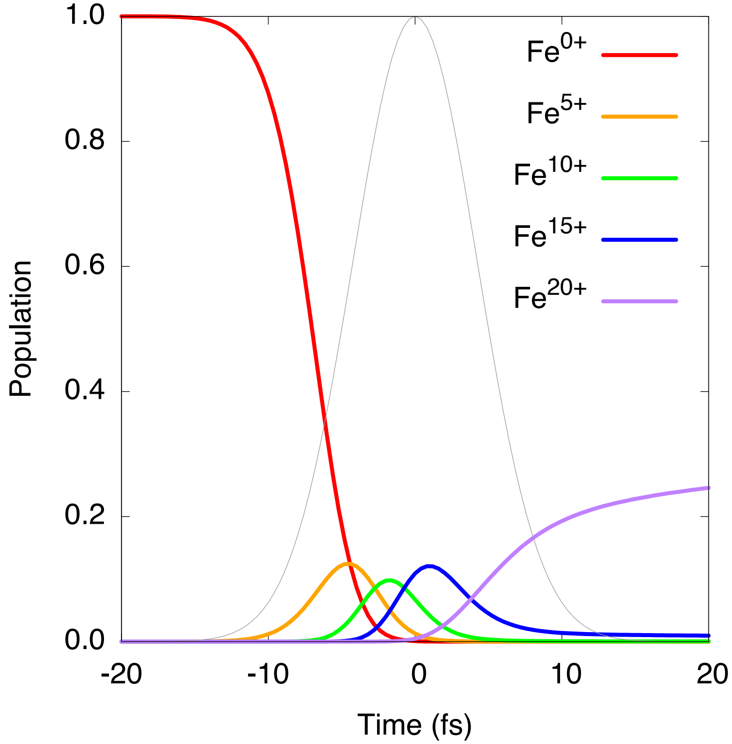
- Growing high-quality crystals is one of major bottlenecks in x-ray crystallography.
- Unprecedented high x-ray fluence from XFEL (×10^6 larger than synchrotron radiation)
- Enough signals from nano-sized crystals and single molecules
- Single-shot molecular imaging: revolutionary impact on structural biology



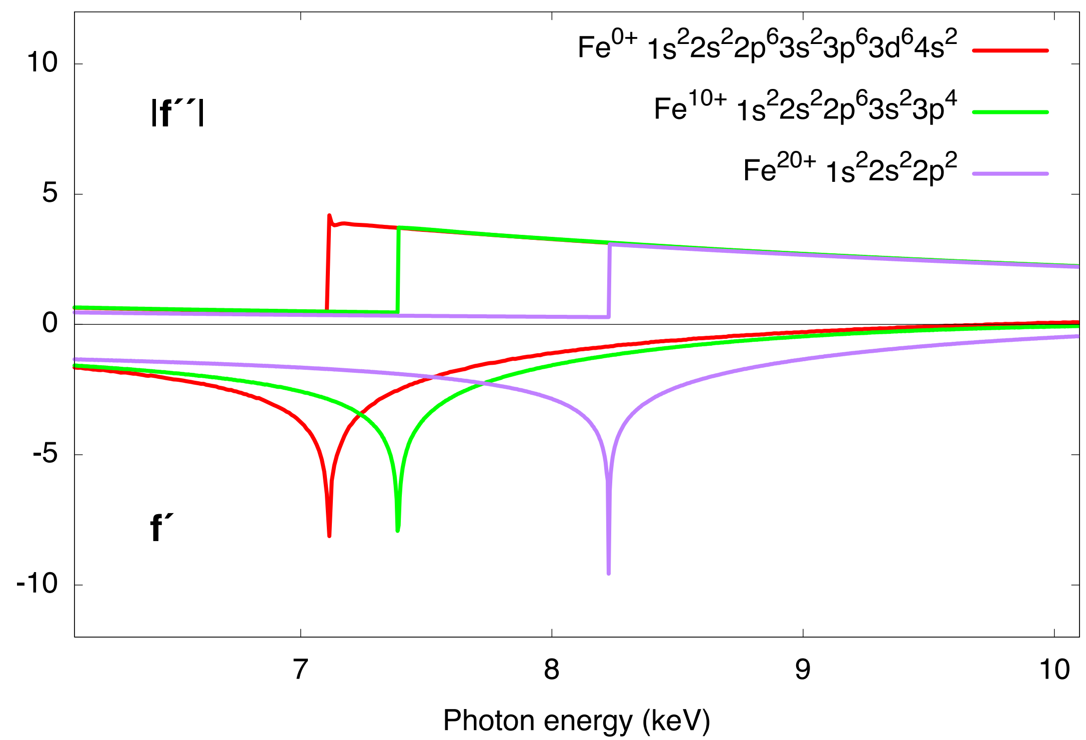
Chapman *et al.*, *Nature Phys.* **2**, 839 (2006).
Figure taken from Gaffney & Chapman, *Science* **316**, 1444 (2007).

Electronic damage to heavy atoms

Population dynamics of Fe charge states during an XFEL pulse (8 keV, 5×10^{12} photons/μm^2, 10 fs FWHM)



Dispersion corrections of atomic form factors of Fe and its ions



Adapted from Son, Chapman & Santra, *PRL* **107**, 218102 (2011).

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Prior speculations regarding MAD at XFEL

- Unavoidable electronic damage, esp. to heavy atoms
- Dramatic change of anomalous scattering for high charge states
- Stochastic electronic damage to heavy atoms would destroy coherent scattering signals in nanocrystals
- MAD would not be an applicable route for phasing at XFEL...?

- We demonstrate the existence of a Karle-Hendrickson-type equation in the high-intensity regime.
- We show that MAD not only works, but also the extensive electronic rearrangements at high x-ray intensity provide a new path to phasing.

Son, Chapman & Santra, *PRL* **107**, 218102 (2011).

Scattering intensity including elec. damage

$$\frac{dI(\mathbf{Q},\omega)}{d\Omega} = \mathcal{F}C(\Omega)\int_{-\infty}^{\infty} dt\, g(t) \sum_I P_I(t) \left| F_P^0(\mathbf{Q}) + \sum_{j=1}^{N_H} f_{I_j}(\mathbf{Q},\omega) e^{i\mathbf{Q}\cdot\mathbf{R}_j} \right|^2$$

$$I = (I_1, I_2, \cdots I_{N_H}), \quad P_I(t) = \prod_{j=1}^{N_H} P_{I_j}(t)$$

$$f_{I_j}(\mathbf{Q},\omega) = f_{I_j}^0(\mathbf{Q}) + f_{I_j}'(\omega) + i f_{I_j}''(\omega)$$

- *P*: protein, *H*: heavy atoms; only heavy atoms scatter anomalously and undergo damage dynamics during an x-ray pulse.
- All changes among N_H heavy atoms are included.
- Heavy atoms are ionized independently.
- Only one species of heavy atoms is considered.

Son, Chapman & Santra, *PRL* **107**, 218102 (2011).

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Generalized Karle-Hendrickson equation

$$\frac{dI(\mathbf{Q},\omega)}{d\Omega} = \mathcal{F}C(\Omega)\Big[\left|F_P^0(\mathbf{Q})\right|^2 + \left|F_H^0(\mathbf{Q})\right|^2 \tilde{a}(\mathbf{Q},\omega) + \left|F_P^0(\mathbf{Q})\right| \left|F_H^0(\mathbf{Q})\right| b(\mathbf{Q},\omega) \cos\Delta\phi^0(\mathbf{Q}) + \left|F_P^0(\mathbf{Q})\right| \left|F_H^0(\mathbf{Q})\right| c(\mathbf{Q},\omega) \sin\Delta\phi^0(\mathbf{Q}) + N_H \left|f_H^0(\mathbf{Q})\right|^2 \{a(\mathbf{Q},\omega) - \tilde{a}(\mathbf{Q},\omega)\}\Big]$$

- MAD coefficients: $a(\mathbf{Q},\omega),\ b(\mathbf{Q},\omega),\ c(\mathbf{Q},\omega),$ and $\tilde{a}(\mathbf{Q},\omega)$
  → measured or calculated with time evolution of config. populations
- 3 unknowns: $\left|F_P^0(\mathbf{Q})\right|,\ \left|F_H^0(\mathbf{Q})\right|,\ \Delta\phi^0(\mathbf{Q})\ [= \phi_P^0(\mathbf{Q}) - \phi_H^0(\mathbf{Q})]$
  → solvable with measurements at 3 different wavelengths.

Son, Chapman & Santra, *PRL* **107**, 218102 (2011).

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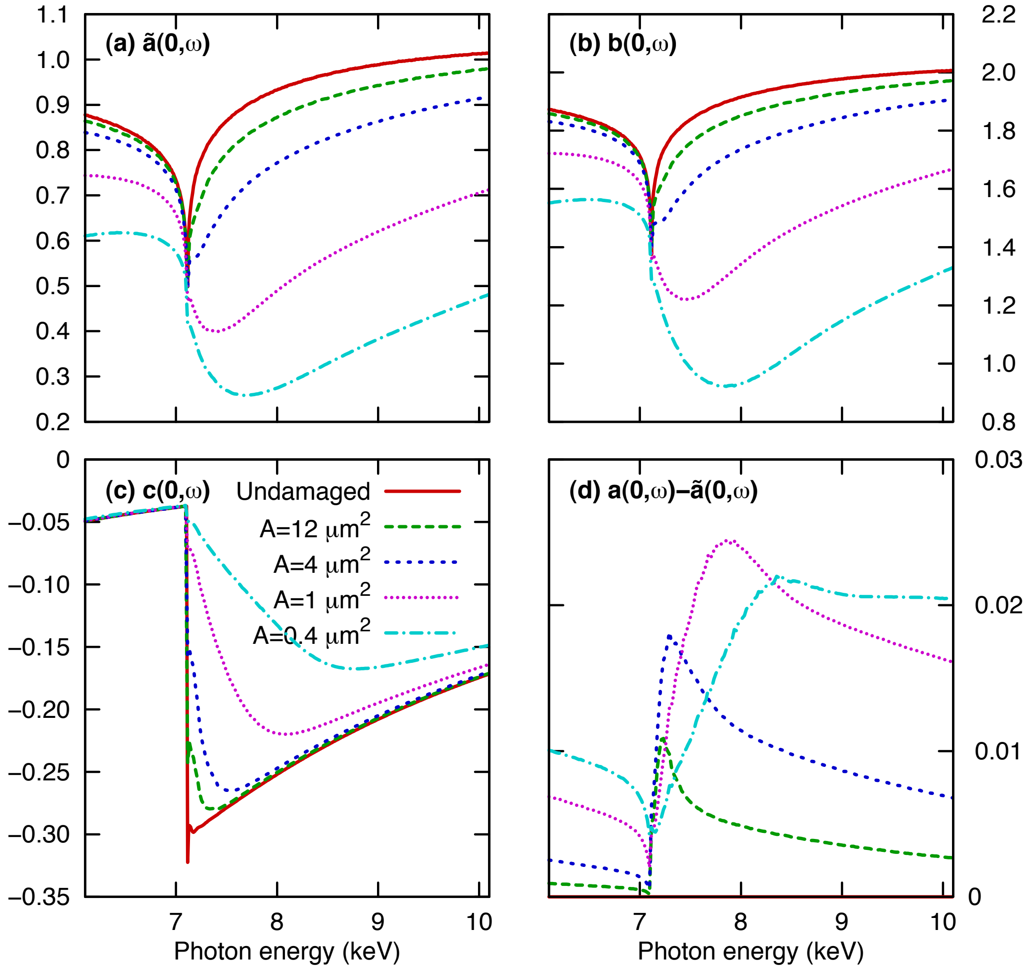
XATOM: x-ray and atomic physics toolkit

- X-ray-induced atomic processes for any given element and configuration
  - photoionization cross section
  - Auger / Coster-Kronig decay rate
  - fluorescence rate
  - coherent x-ray scattering form factor and dispersion correction
  - shake-off branching ratio
- Rate equation model to simulate ionization and relaxation dynamics
- Applications
  - Nonlinear x-ray absorption processes; *PRL* **106**, 083002 (2011); *PRA* **85**, 023414 (2011)
  - Charge distribution analysis of noble gases in XFELs; Rudek *et al.*, submitted
  - Photoelectron / Auger / fluorescence spectra; Son & Santra, in preparation
  - Scattering with electronic damage dynamics at high intensity; *PRA* **83**, 033402 (2011)
  - Multi-wavelength anomalous diffraction at high intensity; *PRL* **107**, 218102 (2011)

MAD coefficients

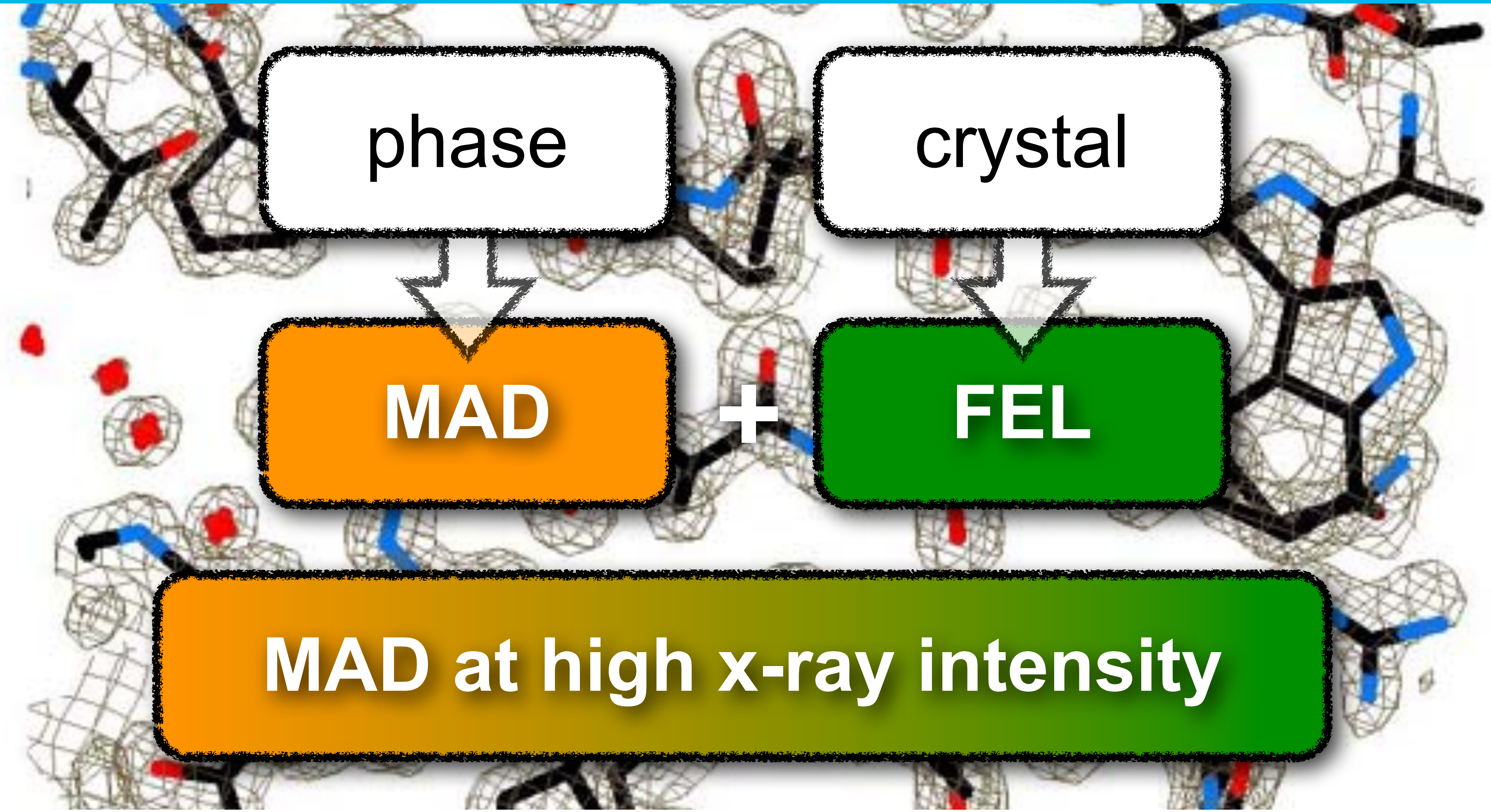
Fe in an x-ray pulse of 2×10^{12} photons and 10 fs FWHM



- calculated by XATOM
- bleaching effect: minimum deepened and edge broadened
- **MAD works**: enhanced contrast at different wavelengths
- **alternative phasing method** similar to SIR (single isomorphic replacement) or RIP (radiation-damage induced phasing)

Son, Chapman & Santra, *PRL* **107**, 218102 (2011).

Conclusion



Acknowledgment

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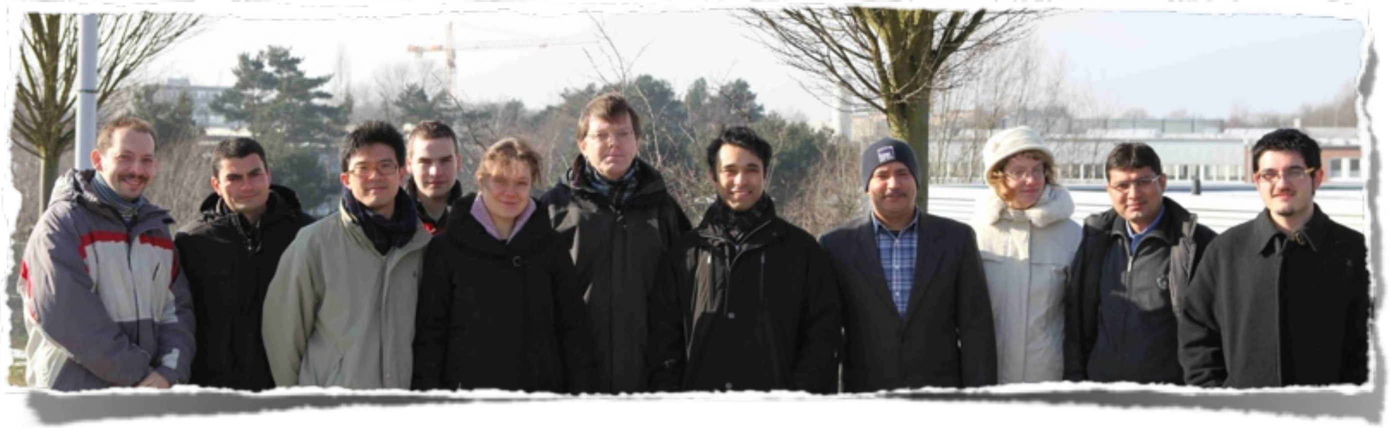

Thank you for your attention!