Final Technical Report, DOE Grant DE-SC0016494
"Nonlinear X-ray Optics"
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Prepared by Matthias Fuchs, PI
University of Nebraska – Lincoln
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1. Introduction

Novel X-ray free-electron lasers (XFELs) are capable of producing radiation with unprecedented properties. Specifically, their ultrashort coherent X-ray pulses can generate extreme peak intensities where ordinary rules of light-matter interaction may no longer apply, and nonlinear processes start to become important. XFELs have made it possible to observe some of the most important coherent *non*-sequential nonlinearities, including X-ray - optical sum frequency generation (SFG)[1], X-ray second harmonic generation (XSHG)[2], two-photon absorption (TPA)[3] and nonlinear two-photon Compton scattering (2PCS)[4]. In particular, the 2PCS experiment has led to unexpected results, namely the observation of a substantial anomalous red shift in the energy of photons generated by nonlinear two-photon X-ray Compton scattering in beryllium. The energy shift is in addition to the predicted nonlinear Compton shift and was neither expected from extrapolations from linear X-ray interactions nor from nonlinear effects at optical wavelengths. Our results suggest a novel nonlinear scattering mechanism that can only be observed at high fields at X-ray wavelengths, where the photon energy is a significant fraction of the electron rest mass (and thus a significant momentum transfer to the electron occurs during the scattering) and where the interaction is not dominated by the quiver motion of the electron in the field (ponderomotive potential) as is usually the case at longer (optical) wavelengths.
The goal of this research project was the investigation of fundamental nonlinear X-ray - matter interactions. As these processes are typically weak, part of this research is the exploration of more efficient nonlinear X-ray processes by studying novel mechanisms including solid-state effects, the assistance of optical radiation and novel phase-matching techniques. These experiments require extremely large X-ray field strengths, such as produced by XFELs. Nonlinear X-ray effects can lead to important applications in many research fields. For example, it could lead to instantaneous plasma diagnostics for materials in extreme conditions, as a method for combining atomic-scale structural sensitivity with chemical specificity, or as a probe of electron dynamics in solids on the attosecond (1 as = 10^{-18} s) time- and Ångstrom (10^{-10} m) length scales. In addition, a detailed understanding of nonlinear X-ray matter interactions is crucial for understanding and extending the limits of structural determination at high intensity such as in serial femto-crystallography. The results could have a profound impact on advanced XFEL light sources such as the LCLS-II.

2. Research Accomplishments

a. ***Non-parametric Two-Photon Hard X-ray Scattering,*** B. Kettle, M. Trigo, M. Kozina, T. Henighan, E. Gamboa, S. Ghimire, J. Hastings, S. Glenzer, D. Reis, M. Fuchs (manuscript in preparation)

The first observation of nonlinear Compton scattering has resulted in an unexpected result: the energy of the generated photon from the simultaneously nonlinear scattering of two 9 keV X-ray photons in a beryllium target was measured to be significantly lower than expected. More specifically, the observed spectrum is redshifted from 18 keV by ~800 eV *in addition* to the expected nonlinear Compton shift. This energy shift is incompatible with the approximation of electrons interacting as quasi free in solids (impulse approximation) for hard X-ray – matter interactions far from atomic resonances. The experiment was performed at extremely high X-ray intensities of ~4×10^{20} W/cm^2.

In order to further investigate this effect we have performed a more detailed study. Part of the experiment was extending the measurement of the nonlinear signal into the forward scattering direction. In addition to the angular distribution, we were also able to extend the lower bound of the additional energy redshift to >2 keV by simultaneously investigating the effect for a wider photon energy range of the incoming beam. Through linear Compton scattering spectroscopy, we were able to infer the temperature of the sample during the interaction. An additional redshift of 800 eV requires an extremely hot plasma temperature with an electronic temperature of kT > 320 eV. The spectrum of the linear Compton scattering does not show a significant broadening, which indicates that the there is no appreciable heating (kT < 10 eV) during the interaction. The unexpected small temperature can be explained by the X-ray interaction generating ~10 keV photoelectrons that propagate outside of the 100 nm focus before depositing most of their energy. The experiment also included different target materials, namely a metal (Be) and dielectric (diamond). The observed emission pattern has a double-peaked shape with an asymmetry in intensity peaked at higher (backward) scattering angles. The asymmetry is increasing with increasing intensity. Although a quadrupole-like pattern is expected for a free-electron interaction, the position of the peaks and the minimum cannot be explained by a free-electron model. An initial model of this process consists of a previously unobserved scattering mechanism that includes the whole atom in the process. In this model, the missing momentum and energy can be transferred to the third body. The process occurs through pA and A^2 scattering processes via a virtual intermediate electronic state, where p is the momentum operator and A the electromagnetic vector potential. However, the observed angular distribution can also not be explained by a simple model that uses the scattering from a virtual intermediate electronic state following photo-ionization.

b. ***Nonlinear resonant x-ray Raman scattering,*** Johann Haber, Andreas Kaldun, Samuel W. Teitelbaum, Alfred Q. Baron, Philip H. Bucksbaum, Matthias Fuchs, Jerome B. Hastings, Ichiro Inoue, Yuichi Inubushi, Dietrich Krebs, Taito Osaka, Robin Santra, Sharon Shwartz, Kenji Tamasaku, and David A. Reis (submitted to Phys. Rev. Letter)

We report on the observation of a comparably strong nonlinear signal through the interaction of two photons with energy near the K absorption edge in Fe. The cross sections are approximately six orders of magnitude higher than what was expected from previous experiments far from atomic resonances in Be. The cross section strongly increases as the photon energy is increased above the K edge. This is in contrast to Cu and Al targets where at the same photon energies (around 7.1 keV) the cross sections are significantly smaller than in Fe and had varied only little as a function of with photon energy. This is an indication that the whole atom participates in the process rather than a free-electron interaction. We have measured the signal as a function of incoming photon energy ranging from below the K edge to well above. The spectrum of the observed signal is very rich. The signal rises quadratically with the incoming intensity, consistent with two-photon excitation. The spectrum of emitted high-energy photons comprises multiple Raman lines that disperse with the incident photon energy. Upon reaching the double K-shell ionization threshold, the signal strength undergoes a significant rise. Above this threshold, the lines cease dispersing, turning into florescence lines with energies much greater than obtainable by single electron transitions, and additional Raman lines appear. We attribute these processes to electron-correlation mediated multielectron transitions involving double-core hole excitation and various two-electron de-excitation processes to a final state involving one or more L and M core-holes. Despite this progress, the detailed mechanism of these fundamental nonlinear processes is still not fully understood, neither far from resonance, nor near resonance.

c. ***Multiple Fourier Component Analysis of X-ray Second Harmonic Generation in Diamond,*** Chakraborti, P., Senfftleben, B., Kettle, B., Teitelbaum, S. W., Bucksbaum, P. H., Ghimire, S., Hastings, J. B., Liu, H., Nelson, S., Sato, T., Shwartz, S., Sun, Y., Weninger, C., Zhu, D., Reis, D. A. & Fuchs, M. (arXiv:1903.02824 2019, in preparation for New Journal of Physics)

We report systematic studies to investigate the physics behind X-ray second harmonic generation (XSHG). In particular, considering the results obtained from two-photon Compton scattering (TPCS), we are exploring any signs of a deviation from the quasi-free electron model. The experiment is performed at ~4 orders of magnitude lower intensities than the TPCS experiment. This will also allow us to explore a lower limit at which the impulse approximation breaks down and compare these findings to the TPCS results (in which case the impulse approximation has broken down). To this end we have performed experiments at LCLS to observe the angle-dependence of the process with high statistics. Clear XSHG signals have been obtained for phase-matching conditions including the reflections from the [220], [111], [11-1], [00-4], [660], [113], [331] and [771] diamond lattice planes. Due to a wide range of scattering geometries, it is possible to compare different nonlinear polarization terms as the source of the signal with simulations. Our simulations are based on the quasi-free electron model. They agree reasonably well with the

experimental observation, except for the width of the crystal rocking curves. Rocking curves for each reflection have been measured and their widths do not significantly change as a function of intensity. However, the curves are wider than expected from simulations and tabulated Darwin widths.

d. ***Scientific Opportunities with an X-ray Free-Electron Laser Oscillator (XFELO),*** B Adams, G Aeppli, T Allison, A. Baron, P. Bucksbaum, A. Chumakov, C. Corder, S. Cramer, S.DeBeer, Y. Ding, J. Evers, J. Frisch, M. Fuchs, G. Grübel, J. Hastings, C. Heyl, L. Holberg, Z. Huang, T. Ishikawa, A. Kaldun, K. Kim, T. Kolodziej, J. Krzywinski, Z. Li, W. Liao, R. Lindberg, A. Madsen, T. Maxwell, G. Monaco, K. Nelson, A. Pálffy,G. Porat,W. Qin, T. Raubenheimer, D. Reis, R. Röhlsberger, R. Santra, R. Schoenlein, V. Schünemann, O. Shpyrko, Y. Shvyd'ko, S. Shwartz, A. Singer, S. Sinha, M. Sutton, K. Tamasaku, H. Wille, M. Yabashi, J. Ye, D. Zhu (arXiv:1903.09317**)**

We have studied opportunities for an X-ray Free-Electron Laser Oscillator (XFELO) in the field of nonlinear X-ray – matter interactions. The XFELO characteristics provide exciting opportunities in X-ray nonlinear optics and coherent spectroscopy. Its narrow bandwidth, high coherence, and widely tunable photon energy range are features of particular interest in nuclear nonlinear spectroscopy. The increased coherent bandwidth (i.e. shorter pulses) and peak power of an XFELO would be of interest for coherent electronic and vibrational spectroscopies. These applications could exploit the possibility of tailoring the electric-field temporal profile spanning eV bandwidths. The XFELO characteristics are well suited for a variety of two-photon processes, including X-ray parametric down-conversion (PDC) and various up- conversion processes. Both can involve lower - frequency components in addition to X-rays. This allows the electronic and/or lattice modulations induced through a lower-frequency resonance to be studied with atomic spatial resolution given by the X-ray wavelength because the frequency-shifted signal is diffracted from the crystal lattice. These processes can also be stimulated in which case they are referred to as sum and difference frequency generation. This provides access to the atomic-scale polarization arising from the induced local fields, and not just the long- wavelength dielectric response.

e. ***Roadmap of Ultrafast X-ray Atomic and Molecular Physics: Hard X-ray Nonlinear Optics,*** M. Fuchs and D. A. Reis, *J. Phys. B* **51**, 3 (2018).

The generation of second harmonic radiation by Franken et al in 1961 shortly after the invention of the laser is widely viewed as the birth of nonlinear optics[5]. The ubiquity of bright optical laser sources coupled with theoretical treatments of light–matter interactions rapidly advanced the field. The field of x-ray nonlinear optics got its start only a decade after Franken's seminal experiment. In 1971, Eisenberger and McCall[6] observed the first nonlinear effect at hard x-ray wavelengths, namely spontaneous parametric down conversion (PDC) of one 17 keV x-ray into two near 8.5 keV photons in a Be crystal using an x-ray tube as the source. In these experiments,

down- converted photon pairs were produced at a maximum rate of about one per hour. The development of significantly more brilliant storage-ring based x-ray sources allowed for much higher rates, leading to a better understanding of x-ray PDC[7]. It also led to new applications, such as the visualization of local induced charge densities in a crystal with atomic spatial resolution[8]. However, nonlinear effects in the hard x-ray regime that involve the simultaneous interaction of multiple incident photons have remained elusive even at the brightest synchrotron sources due to vanishingly small susceptibilities at high frequencies. Only with the billion-fold increase in peak brightness of hard XFELs and with focused intensities approaching those of the most intense optical sources has it become possible to observe multiphoton processes at x-ray wavelengths. First experiments demonstrated that the peak x-ray flux of the LCLS XFEL is sufficient to saturate atomic inner-shell absorption at soft x-ray wavelengths within a few femtoseconds. These experiments were followed by seminal experiments at the LCLS and SACLA XFELs that demonstrated fundamental nonlinear multiphoton interactions at hard x-ray wavelengths. This includes nonsequential two-photon K-shell absorption[3,9], phase-matched sum frequency generation[1], second harmonic generation[2] and two-photon Compton scattering (2PCS)[4]. While the former three experiments match theoretical predictions reasonably well, an anomaly was observed in 2PCS involving an excessive red-shift in the energy of the nonlinearly generated photons compared to what was expected in the quasi-free-electron (impulse) approximation. This discovery demonstrates that our fundamental understanding of x-ray matter interactions is still incomplete. We review the status of the field and the current and future challenges as well as the required advances in science and technology to meet the challenges.

3. Publications from project

- ***Non-parametric Two-Photon Hard X-ray Scattering,*** B. Kettle, M. Trigo, M. Kozina, T. Henighan, E. Gamboa, S. Ghimire, J. Hastings, S. Glenzer, D. Reis, M. Fuchs (manuscript in preparation)

- ***Nonlinear resonant x-ray Raman scattering,*** Johann Haber, Andreas Kaldun, Samuel W. Teitelbaum, Alfred Q. Baron, Philip H. Bucksbaum, Matthias Fuchs, Jerome B. Hastings, Ichiro Inoue, Yuichi Inubushi, Dietrich Krebs, Taito Osaka, Robin Santra, Sharon Shwartz, Kenji Tamasaku, and David A. Reis (submitted to Phys. Rev. Letter)

- ***Angularly-resolved X-ray Second Harmonic Generation,*** Chakraborti, P., Senfftleben, B., Kettle, B., Teitelbaum, S. W., Bucksbaum, P. H., Ghimire, S., Hastings, J. B., Liu, H., Nelson, S., Sato, T., Shwartz, S., Sun, Y., Weninger, C., Zhu, D., Reis, D. A. & Fuchs, M. (arXiv:1903.02824 2019, in preparation for New Journal of Physics)

- ***Scientific Opportunities with an X-ray Free-Electron Laser Oscillator (XFELO),*** B Adams, G Aeppli, T Allison, A. Baron, P. Bucksbaum, A. Chumakov, C. Corder, S. Cramer, S.DeBeer, Y. Ding, J. Evers, J. Frisch, M. Fuchs, G. Grübel, J. Hastings, C. Heyl, L. Holberg, Z. Huang, T. Ishikawa, A. Kaldun, K. Kim, T. Kolodziej, J. Krzywinski, Z. Li, W. Liao, R. Lindberg, A. Madsen, T. Maxwell, G. Monaco, K. Nelson, A. Pálffy,G.

Porat,W. Qin, T. Raubenheimer, D. Reis, R. Röhlsberger, R. Santra, R. Schoenlein, V. Schünemann, O. Shpyrko, Y. Shvyd'ko, S. Shwartz, A. Singer, S. Sinha, M. Sutton, K. Tamasaku, H. Wille, M. Yabashi, J. Ye, D. Zhu (arXiv:1903.09317**)**

- ***Roadmap of Ultrafast X-ray Atomic and Molecular Physics: Hard X-ray Nonlinear Optics,*** M. Fuchs and D. A. Reis, *J. Phys. B* **51**, 3 (2018).

4. Invited presentations

- **Nonlinear Hard X-ray Optics,** Gordon Research Conference, Easton, MA (2019)
- **Probing strong-field QED in electron-photon interactions,** DESY, Hamburg, Germany (2018)
- **Scientific opportunities with the Compact XFEL: Attosecond electron dynamics to chemical physics**, Arizona State University, Tempe AZ (2018)
- **LCLS-II-HE "First Experiments" workshop,** subgroup leader, SLAC National Accelerator Laboratory, CA (2017)
- **Advances in Free-Electron Laser Science,** Hamburg, Germany (2017)
- **Symposium on Imaging and Controlling Ultrafast Dynamics of Atoms, Molecules, and Nanostructure,** Kansas State University, Manhatten KS (2017)
- **X-ray Free-Electron Laser Oscillator XFELO Science Workshop**, SLAC National Accelerator Laboratory, CA (2016)
- **OSA High-Intensity Lasers and High-Field Phenomena (HILAS),** Long Beach, CA (2016)

5. Students and postdocs involved in this project

Graduate Students: Björn Senfftleben (100%), MSc 2017; Priyanka Chakraborti (100%), MSc 2020; Kyle Jensen (20%)
Undergraduate students: Vida-Michelle Nixon, now at Univ. of Toronto
Postdoc: Brendan Kettle, now at Imperial College, UK; Özgür Culfa, now at Karamanoglu Mehmetbey University, Turkey

6. Bibliography

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