Non-equilibrium optical response of Zinc Oxide

X-ray transient absorption spectra at the Zn K-edge in ZnO: dependence on pump and time evolution

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In Short

- Computation of the non-thermal X-ray transient absorption (XTA) spectra with pump fluences on the picosecond timescale;
- Investigation of the transient evolution of non-thermal XTA spectra from attoseconds to femtoseconds;
- Decomposion of the non-thermal XTA spectra into Pauli blocking and core-hole screening contribution.

Zinc oxide (ZnO) has emerged as an attractive semiconducting oxide over the past few decades. Its direct wide bandgap of 3.3 eV along with a substantial exciton binding energy of 60 meV [1], leads to a widespread application in the field of optoelectronics. Understanding the optical properties of ZnO is essential for its fundamental characterization and applications.

X-ray transient absorption (XTA) spectroscopy is one of the most crucial techniques for measuring the optical properties of ZnO. It utilizes a "pump-probe" approach, where a laser pulse (pump) initiates a transient process, followed by an X-ray pulse (probe) at varying time delays to investigate the transient electronic and geometric structures of ZnO in response to the pump. Over the past decade, XTA spectroscopy has evolved significantly, from an initial concept to a widely accepted technique for characterizing local electronic and nuclear structures.

Despite the profuse research about the XTA spectra of ZnO in the last decades, there are still open questions on separating the thermal (lattice vibration) and non-thermal (electronic) contribution to the XTA spectra. Our collaborators pioneer an experimental technique to isolate the non-thermal and thermal XTA spectra at a time delay of 100 ps [2], shown in Fig.1. The non-thermal XTA spectra display two negative features at 9.661 keV and 9.6665 keV followed by a prominent positive feature with a shoulder at 9.671 keV, and their amplitudes increase with the rising pump fluences. They propose the large negative features at 9.661 keV and 9.6665 keV come from core-hole screening [2]. However, there is a lack of investigation to reveal the origin of non-thermal XTA spectra and decompose them explicitly.

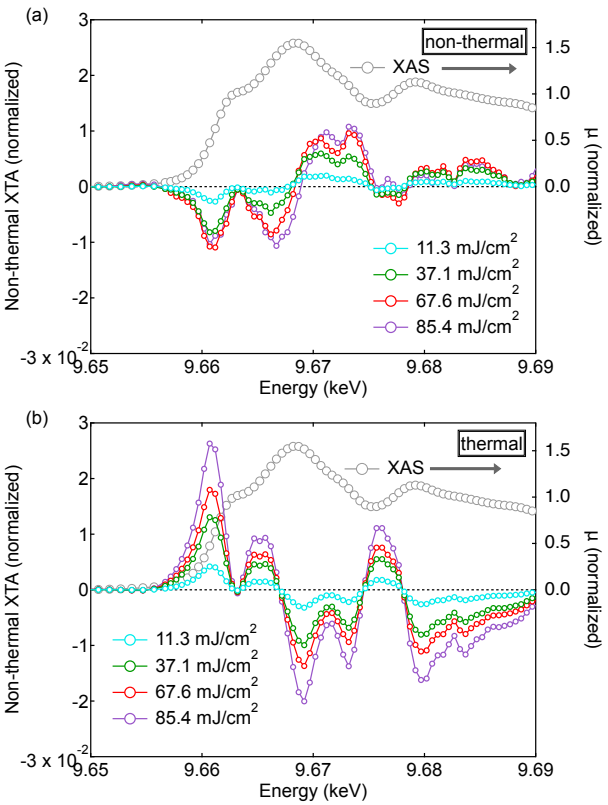

Figure 1: *The evolution of (a) non-thermal, and (b) thermal contributions to the XTA spectra at the Zn K-edge of ZnO in experiments with excitation fluences. The amplitude of XTA spectra is normalized to the X-ray absorption (XAS) spectra edge jump.*

It is therefore essential that the theoretical XTA spectra are needed to be calculated accurately to give insights into the features of non-thermal XTA spectra. To date, various approaches have been developed to calculate steady-state X-ray absorption (XAS) spectra, such as linear response time-dependent density functional theory (TDDFT), many-body perturbation theory, etc, and overlooking time-resolved absorption spectra which are crucial to reflect dynamic features. Here, we pioneer a new approach to compute the time-resolved non-thermal XTA spectra and decompose it to different contributions, consequently, investigating their evolution under varying pump fluences at different time delays.

All calculations are performed by the all-electron, full-potential computer package `exciting` [3], which employs the linear augmented plane wave plus local orbital methods. Its all-electron approach enables us to capture core-excitation features. This package not only encompasses ground-state calculations but primarily focuses on the properties of

excited states. It includes real-time time-dependent density functional theory (RT-TDDFT) with various time-dependent exchange-correlation functionals. It can also compute the XAS spectra in steady-state through the solution of the Bethe–Salpeter equation (BSE), allowing for the characterization of strongly bound excitons. Building upon previous implementations, we have developed a novel framework for computing XAS in excited states by integrating the occupation factors from RT-TDDFT runs, as depicted in the workflow schema (Fig.2).

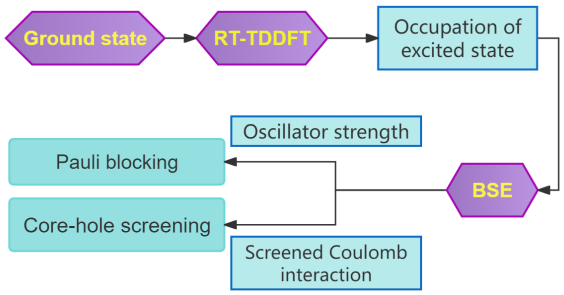

Figure 2: *Workflow for computing and decomposing the non-thermal XTA spectra.*

Starting with the ground-state calculation, we obtain the electron density and potential necessary for the time evolution in a subsequent RT-TDDFT run. During the RT-TDDFT run, we capture the excited-state occupations. They are adopted as constraints to the solution of the BSE to compute the XAS spectra in the excited state. The non-thermal XTA spectra are derived from the difference between the excited and ground state XAS spectra. They consist of two main contributions: Pauli blocking and core hole screening. Pauli blocking occurs when the potential final states of dipole transitions are filled so that an incoming electron can no longer make this transition. Core-hole screening reflects the response of excited electrons to core excitations. To isolate the Pauli blocking effect, we calculate the oscillator strength using the excited-state occupations. For the core-hole screening effect, we use the excited-state occupations to calculate the screened Coulomb interaction.

Based on this approach, we outline three objectives for this project:

- **Computation of the non-thermal XTA spectra with pump fluences on the picosecond timescale.**
  The experimenter observed an increased amplitude of non-thermal XTA with rising pump fluences, yet providing a clear explanation for this trend based on experimental data is challenging. Our goal is to compute the non-thermal XTA as pump fluences rise and interpret its relationship with fluences from a theoretical point of view.
- **Investigation of the transient evolution of non-thermal XTA spectra from attoseconds to femtoseconds.**
  The experiment measures the non-thermal XTA spectra on picosecond timescales, which is not sufficient to capture ultrafast dynamics that occur on attosecond to femtosecond timescales. However, the generation of X-ray pulses and detection at shorter timescales requires a high demand for equipment and precision. We aim to calculate the non-thermal XTA spectra from attoseconds to femtoseconds, providing a prediction for the experiment.
- **Exploration of the non-thermal XTA spectra components, focusing on the contributions from Pauli blocking and core-hole screening.**
  This objective is to distinguish between Pauli blocking and core-hole screening contributions on non-thermal XTA spectra, identify the predominant factor influencing the spectra, and reveal how they evolve with varying pump fluences.

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More Information

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[2] Thomas C. Rossi, Conner P. Dykstra, et al. *Nano Lett.* **21**, 9534 (2021). doi: https://doi.org/10.1021/acs.nanolett.1c02865

[3] Andris Gulans, Stefan Kontur, et al. *J. Phys.: Condens.Matter* **26**, 363202 (2014). doi: 10.1088/0953-8984/26/36/363202

Project Partners

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