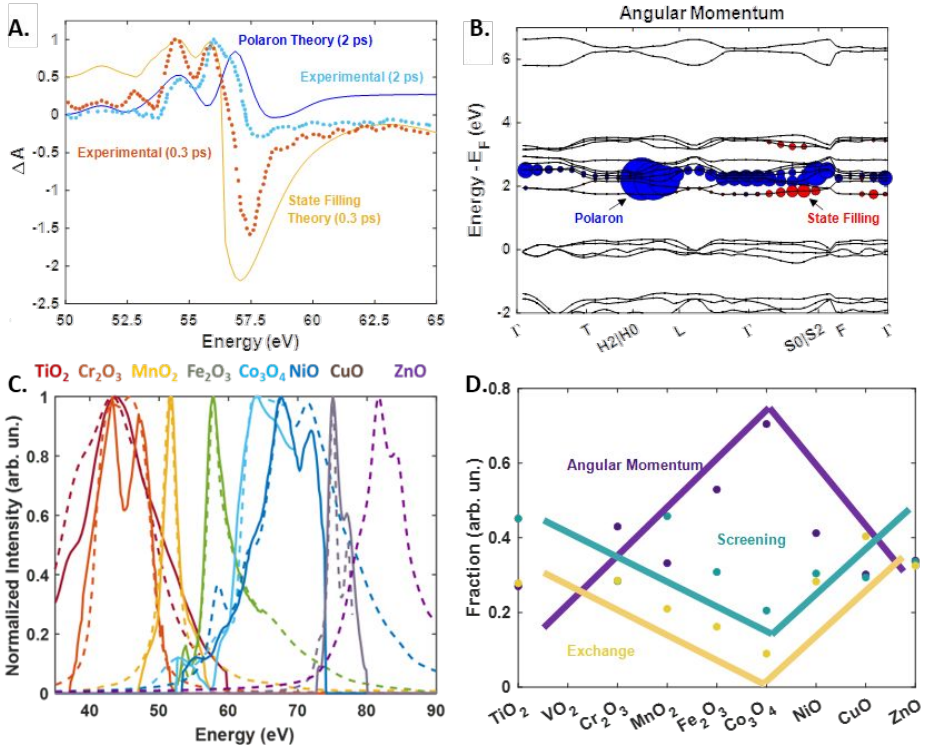
Ab Initio Prediction of Excited State and Polaron Effects in Transient X-ray Measurements of Metal Oxides



(A) Theoretically predicted differential absorption for polarons and excited state transitions in α-Fe_2O_3. **(B)** Angular momentum and screening contributions for the polaron excited state. **(C)** Prediction of the ground state spectra for a range of metal oxides in the XUV region. **(D)** Projection of which X-ray Hamiltonian component dominates the spectrum and the related excited state changes.

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Scientific Achievement:

An ab initio, Bethe-Salpeter equation (BSE) approach was developed that incorporates photoexcited state effects into the calculation of extreme ultraviolet (XUV) spectra for arbitrary materials systems. The accuracy of the approach was proven by calculating the XUV absorption spectra for the ground, photoexcited, and polaron states of α-Fe_2O_3 and other metal oxides. The theoretical approach also allows for the projection of the core-valence excitons and X-ray transition Hamiltonian components onto the band structure.

Significance and Impact:

The projection of the core-valence excitons onto the band structure gives a physical intuition about the origins and nature of the transient XUV spectra. A route to extracting electron and hole energies is even shown possible in highly angular momentum split XUV peaks. This method is easily generalized to K, L, M, and N edges to provide an approach for analyzing any transient X-ray absorption or reflection data.

Research Details:

- The theoretical approach is based on modifications to the Obtaining Core Excitations from *Ab initio* electronic structure and the NIST BSE solver (OCEAN) code
- Decomposition of BSE Hamiltonian into angular momentum, screening, and exchange
- Modeling of metal oxides, corresponding to the charge transfer and polaron states

1) Klein, I. M.; Liu, H.; Nimlos, D.; Krotz, A.; Cushing, S. K. *Ab Initio* Prediction of Excited-State and Polaron Effects in Transient XUV Measurements of α-Fe_2O_3. *J. Am. Chem. Soc.* **2022**, jacs.2c03994. https://doi.org/10.1021/jacs.2c03994.
2) I. M. Klein; A. Krotz; J. M. Michelsen; S. K. Cushing *Ab Initio* Calculations of XUV Ground and Excited States for First-Row Transition Metal Oxides, *J. Phys. Chem. C* **2023,** https://doi.org/10.1021/acs.jpcc.2c06548

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