

Attosecond dispersive soft X-ray absorption fine structure spectroscopy in graphite

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Introduction:

X-ray absorption fine-structure (XAFS) spectroscopy is a powerful element-specific technique, providing electronic and structural information with atomic resolution. Electronic information is extracted from the near-edge XAFS (NEXAFS) spectrum, requiring high spectral resolution to resolve features that occur within a few eV near the absorption edge. Structural information is obtained from the extended XAFS (EXAFS), spreading over several hundred eV above the absorption edge. While XANES and EXAFS are both well-established methods, crucially lacking so far is the capacity to connect electronic with structural information in real-time. Here, we present a decisive step towards such new methodology based on water-window-covering (280 eV to 540 eV) attosecond soft X-ray (SXR) pulses that can simultaneously access electronic and lattice parameters via dispersive XAFS spectroscopy. We demonstrate the novel capabilities of attosecond XAFS (attoXAFS) by identifying the σ^* and π^* orbital contributions to the density of states in graphite simultaneously with the four characteristic bonding distances of graphite's hexagonal lattice. Our work demonstrates the novel concept of attoXAFS as a powerful real-time investigative tool which is equally applicable to the gas-, liquid- and condensed phase.

Results and Discussion:

XAFS spectroscopy on graphite is performed using isolated sub-300 attosecond SXR pulses which are generated via high-harmonic generation in a table-top geometry¹. The SXR pulses are focused onto a 95nm thick graphite sample and the transmitted beam is detected in a home-built spectrograph. The graphite's XAFS spectrum is measured at incidence angles of 0°, 20°, and 40°. For each incidence angle the XAFS spectrum shows a clear rising edge at 292.6±0.3 eV followed by undulations in the absorption spectrum. From symmetry considerations, it is apparent that the edge arises due to the 1s→ σ^* transition. Varying the incidence angle from 0° to 20°, a second peak appears at 285.5±0.3 eV with an amplitude that increases as the incident angle is further increased to 40°. The clear field polarization dependence of the peak at 285.5 eV allows us to identify this as the 1s→ π^* transition since the π^* is formed by carbons's p_z orbital, orientated perpendicular to the sample plane. At 0°, graphite planes are orientated perpendicular to the beam propagation direction, thus the attosecond pulse's linearly-polarized electric field only probes in-plane σ^*

states, consisting of sp^2 hybridized orbitals. These features, measured with the attosecond source, are in excellent agreement with electronic transitions measured at synchrotron light sources².

To deduce information about graphite's bond length, the extended XAFS spectrum is analyzed with the aid of Athena and Artemis software packages. This analysis clearly highlights the scattering contributions from the 1st, 2nd, 3rd and 4th neighboring carbon atoms. Here, bond distances of 1.66 ± 0.03 Å, 2.58 ± 0.12 Å, 2.92 ± 0.03 Å and 4.01 ± 0.10 Å are identified. Again, the results from attoXAFS are in excellent agreement with DFT calculations and carbon K-edge EXAFS measurements conducted at synchrotron sources³.

Conclusion:

This work establishes attoXAFS as a powerful new table-top methodology capable of simultaneously probing electronic states and atomic positions in condensed matter systems. Furthermore, attoXAFS gives access to the characteristic time-scale of electronic motion to study charge migration, electron-electron correlation, electron-nuclear scattering and structural transitions with previously unprecedented attosecond time resolution.

References

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