Probing Molecular Chirality with Nonlinear X-ray Spectroscopies

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Recent advancements in synchrotron and X-ray free-electron laser (XFEL) light sources have opened new avenues for exploring molecular chirality through element-sensitive nonlinear spectroscopies. While traditional techniques like circular dichroism (CD) and sum- and difference-frequency generation (SFG/DFG) have been widely used in the optical regime, extending them to the X-ray domain provides deeper insights into local structural asymmetries by exploiting the element specificity of core orbitals. In this work, we simulate X-ray absorption spectroscopy (XAS), X-ray circular dichroism (XCD), and nonlinear optical/X-ray SFG and DFG (OX SFG/DFG) signals for two prototypical chiral molecules, fenchone and cysteine. Our multi-reference simulations successfully reproduce available experimental data and highlight how novel X-ray spectroscopies enhance sensitivity to molecular asymmetry. We find that XCD spectra exhibit strong asymmetries at chiral centers, while contributions from distant atoms are significantly weaker. Additionally, OX SFG/DFG signals, under fixed resonant optical excitation, show a strong dependence on core transitions and valence excitation energies, enabling the introduction of a two-dimensional chirality-sensitive valence-core spectroscopy. This approach provides new insights into interplay between valence orbitals and local molecular asymmetry. Finally, we estimate the feasibility of such non-linear experiments at XFELs using realistic laser and X-ray pulse parameters. Our results suggest that nonlinear X-ray spectroscopies represent a promising tool for probing the geometric and electronic structures of chiral molecules with unprecedented sensitivity.

Keywords: Chirality, Nonlinear spectroscopy, Fenchone and Cysteine.

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[1]Y. Nam, M. Chergui, L. Young, and J. R. Rouxel, "Linear and nonlinear X-ray spectra of chiral molecules: X-ray Circular Dichroism, Sum and Difference-Frequency Generation of fenchone and cysteine", arXiv:2501.14671 [physics.chem-ph]