Electronic Coherence in Ultrafast X-Ray Scattering by Molecules

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Recent advances in the preparation of intense, ultrafast, and coherent pulses of hard x-rays permit the observation of dynamics in atoms and molecules in real time *via* non-resonant scattering. The elastic component of the scattering signal is well known to provide information about time-dependent changes in the molecular one-electron density as a result of nuclear motion. The inelastic component, in contrast, is usually not considered, as it is commonly assumed that inelastic scattering does not depend on the nuclear geometry and thus time. Contesting the generality of this assumption, we have shown that the inelastic component can be time-dependent as well.[1] Extensive simulations of ultrafast x-ray scattering by a nuclear wave packet in the hydrogen molecule have demonstrated that the inelastic component changed significantly in the course of the nuclear dynamics. Moreover, pulses generated at new X-Ray Free-Electron Laser facilities may enable the detection of a third component in the scattering signal that we have termed *coherent mixed*. It is caused by an intramolecular interference of scattering amplitudes of at least two electronic states that are coherently populated. In their groundbreaking paper, Dixit *et al.* have shown that the ultrafast x-ray scattering signal of an electronic wave packet in the hydrogen atom is not just given by the Fourier transform of its one-electron density.[2] In essence, it is the coherent mixed component that led to the time-dependent signal Dixit and his coworkers have reported.[3] The coherent mixed component was furthermore addressed in seminal work by Mukamel *et al.*, who have demonstrated that the component can carry a distinct signature of non-adiabatic population transfer in the vicinity of an avoided crossing.[4,5] We have recently published the first two-dimensional coherent mixed scattering patterns of a molecule and showed that they provide a direct probe of the degree of electronic coherence.[1] It is thus likely that information beyond pure structural dynamics can be obtained from ultrafast x-ray scattering experiments in future.

References

1. M. Simmermacher, N. E. Henriksen, K. B. Møller, A. Moreno Carrascosa, and A. Kirrander, *Phys. Rev. Lett.* **122** (2019), 073003.
2. G. Dixit, O. Vendrell, and R. Santra, *Proc. Natl. Acad. Sci. U.S.A.* **109** (2012), 11636.
3. M. Simmermacher, N. E. Henriksen, and K. B. Møller, *Phys. Chem. Chem. Phys.* **19** (2017), 19740.
4. M. Kowalewski, K. Bennett, and S. Mukamel, *Struct. Dyn.* **4** (2017), 054101.
5. K. Bennett, M. Kowalewski, J. R. Rouxel, and S. Mukamel, *Proc. Natl. Acad. Sci. U.S.A.* **115** (2018), 6538.