

Theory of X-ray photoelectron diffraction from molecules undergoing an ultrafast photochemical reaction

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Synopsis We present a full-quantum theoretical method to obtain time-dependent X-ray photoelectron diffraction (XPD) profiles combining nuclear wave packet calculation and a multiple-scattering XPD theory. Then, we demonstrate the time-dependent XPD profiles from isolated gas-phase molecules undergoing ultrafast photochemical reactions.

A pump and probe experiment of ultrafast optical laser and X-ray free-electron laser (XFEL) pulse can realize ultrafast X-ray photoelectron diffraction (XPD) measurements. The XPD patterns capture the entire molecular geometry, thus such experiment can track atomic positions during unimolecular photochemical reactions in femtosecond time scale and ångström spatial resolution [1].

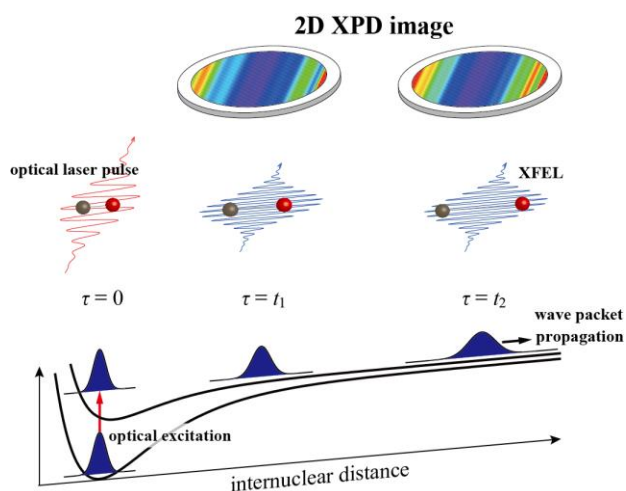


Figure 1. Sketch of an optical laser pump–XFEL probe experimental scheme. An optical laser prepares vibrational wave packets on an excited state. Then, they are probed by means of XPD images with XFEL pulses.

Hence, we theoretically demonstrate the XPD profiles of simple molecules during photochemical reactions, which are controlled by the excitation processes with the optical laser pulses. Under the assumption that a valence electron in the ground state is excited to an excited state, we numerically integrate the time-dependent Schrödinger equation of such excitation process within the Born-Oppenheimer approximation [2]. Then, we calculate the static

XPD amplitude at a certain molecular geometry on the basis of a multiple-scattering XPD theory [3]. Under the assumption that the nuclei are frozen during the probe pulse, the time-resolved XPD profiles with the ultrafast XFEL pulses are obtained as the convolution of the static XPD profiles weighted by the nuclear wave packet over the molecular geometry.

The XPD simulations based on such nuclear wave packet calculations are observed to exhibit characteristic features, which are compared with the XPD profiles due to classical trajectories of nuclear motions.

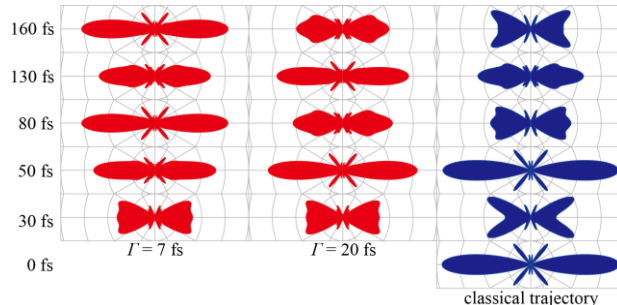


Figure 2. Time-resolved C 1s X-ray photoelectron diffraction (XPD) profiles of CS₂ molecules undergoing bending vibration induced by B-X transition. The delay time are written on the left of the panel. Left: laser intensity of $I_0 = 3.0 \times 10^{11}$ W/cm² with pulse width of $\Gamma = 7$ fs, middle: laser intensity of $I_0 = 3.0 \times 10^{11}$ W/cm² with pulse width of $\Gamma = 20$ fs, and right: a classical trajectory.

References

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