Molecular photodynamics at Free-Electron Lasers

O Plekan

Elettra Sincrotrone Trieste, Area Science Park, 34149 Basovizza, Trieste, Italy

Understanding the nature of molecular dynamics in detail, such as visualization of molecular bond breaking, charge-transfer processes, proton migration, Interatomic Coulombic decay (ICD), photoprotection, ring opening and isomerization phenomena induced by the interaction of photons with matter has become viable with the advent of ultrafast laser pulses [1].

Tabletop lasers spanning wavelengths from the near infrared (NIR), to the X-ray regime with high harmonic generation (HHG) have been widly applied in research on molecular dynamics by implementing pump-probe techniques. The standard pump–probe scheme utilises a pump pulse, which initiates the motion/transformation in the molecule, and a probe pulse which detects these changes by using time delays between the two pulses to capture these dynamics. However, ultrafast pump-probe experiments in the X-ray regime with tabletop lasers are still a significant challenge, due to the low photon flux in the X-ray photon range [2]. Free-electron lasers (FELs) have emerged as a powerful new tool in this quest because of their unique combination of properties such as ultrashort pulse duration, wavelength tunability (in the EUV and XUV range) temporal and transverse coherence, polarization control and high peak power. Pump–probe techniques with short-wavelength FELs have made it possible to employ novel investigations of ultrafast photodynamics in numerous atomic and molecular phenomena at unpecedented spatial (tenths of ångströms) and temporal scales (few femtoseconds).

Here, we discuss a few highlights of FEL-based investigations of ultrafast molecular dynamics targeting some isolated biomolecules: thymine [3], acetylacetone [4], indole [5] and thiophenone [6]. These studies illustrate the advantages of FELs: access to core excitations, greatly improved signal to noise, and for valence ionization, measurement of a ide range of valence states. In case of [4-6], time-resolved photoelectron-photoion measurements have been performed using short-pulse, narrow-bandwidth extreme ultraviolet radiation provided by the seeded FEL FERMI [7], while data from [3] was obtained at the Linac Coherent Light Source (LCLS) FEL facility [8].

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