Imaging Molecular Structure and Dynamics utilizing X-ray Free-Electron-Laser Sources

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***Abstract*—Imaging controlled molecules with ultrashort x-ray pulses from free-electron lasers enables the recording of "molecular movies", i.e., snapshots of molecules at work, with spatial (picometer) and temporal (femtosecond) atomic resolution.**

Hard-x-ray free-electron lasers (FELs) provide femtosecond-duration pulses of x-rays with unprecedented brilliance [1], [2]. These enable the study of ultrafast chemical dynamics of isolated molecules in the gas phase using diffractive-imaging methods [3]–[7]. We exploit various imaging approaches to understand the intrinsic molecular structure and function, which is at the very heart of the chemical and molecular sciences.

Experiments that allow for the creation of structurally pure samples and, subsequently, for the investigation of their intrinsic molecular dynamics and chemical function have developed tremendously over the last few decades, although "there's plenty of room at the bottom" – for better control as well as for further applications. We detail the use of inhomogeneous electric fields for the manipulation of neutral molecules in the gas-phase, i.e., for the separation of complex molecules according to size, structural isomer, and quantum state [8]–[12]. These quantum-state-selected samples allow for very strong degrees of alignment and orientation [9], [13]–[17]. The produced ensembles of structurally sorted and fixed-in-space molecules are well-suited for imaging experiments, as the availability of many identical molecules in the camera's frame of reference allows for direct, experimental averaging of the recorded signal until it is above noise.

We have performed a number of imaging experiments at the Linac Coherent Light Source (LCLS) at SLAC [2] and the Free-Electron Laser in Hamburg (FLASH) at DESY [18]. These include the direct x-ray-diffractive imaging of aligned isolated gas-phase molecules [19], [20] and photoelectron-holography approaches, which are implemented as imaging of molecular-frame photoelectron angular distributions (MFPAD) [21]–[23]. In these first benchmark imaging experiments, we have exploited cold molecular beams from state-of-the-art pulsed valves. These beams were further purified using the electric deflector [24], which spatially disperses the beam according to the molecules' quantum states and separates the molecules from the atomic seed gas. The quantum-state selected samples were laser aligned or mixed-field oriented using nanosecond-pulsed Nd:YAG lasers or stretched pulses from amplified Ti:Sapphire laser systems. The latter allows to generate strong alignment and orientation at full FEL repetition rates [15], [25].

Here, we report on two approaches to image these controlled samples: first, we observe the wide-angle scattering patterns from these molecules. The images recorded on pixelated detectors are the incoherent sums of the coherent-diffractive-imaging (CDI) patterns of the (identical) isolated gas-phase molecules [6], [19], [20]. For the controlled samples employed, this corresponds to a single-molecule pattern with an enhanced signal-to-noise ratio. Alternatively, we have observed the MFPADs following photoionization of these samples. These MFPADs show holographic structures due to the interference of the direct and the scattered parts of the outgoing-electron wave. Especially in the case of core excitations above an absorption edge, e.g., F($1s$) photoionization, this hologram provides chemical sensitivity for probing of the local structure around the ionized atom [21]–[23]. These experiments will be compared to modern imaging experiments utilizing table-top laser systems, such as MFPAD measurements following strong-field ionization [26], [27], laser-induced electron diffraction [28], or high-harmonic spectroscopy [29].

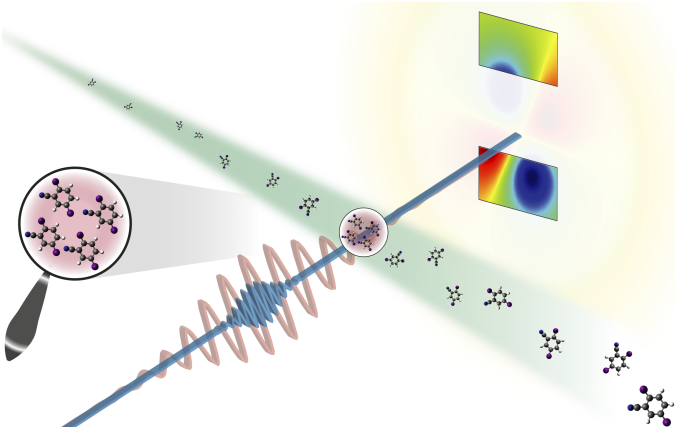

Fig. 1. Sketch of the experimental setup for the atomically-resolved imaging of controlled isolated gas-phase molecules [19].

Moreover, coincidence ion imaging under similar conditions allows to investigate the ultrafast electronic dynamics of x-ray photoionized dissociating molecules [30], [31].

We summarize current experiments and analyze the feasibility of atomically resolved imaging of ultrafast molecular dynamics. Based on experience from these first experiments, design criteria and experimental approaches for x-ray diffractive imaging of isolated gas-phase molecules are discussed [32]. We propose that these experiments can be performed as secondary, parasitic experiments, upstream of and in-line with more x-ray-intensity demanding primary experiments.

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