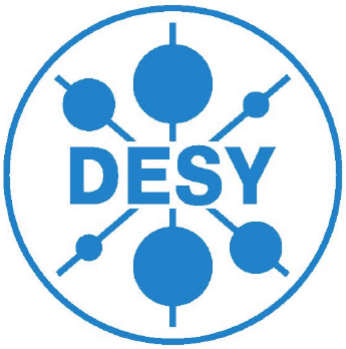

Ultrafast Molecular Imaging Group, DESY Hamburg

Work report

by

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Abstract

This report presents the experimental methodology for an ultrafast molecular imaging technique, based on an pump-probe-experiment on aligned molecules, in the X-ray region using FEL and synchrotron facilities. Additionally, a test-setup for the test of an ion-spectrometer and the study of the fragmentation channels of small organic molecules after electron impact ionization is presented.

Contents

1 Introduction

Ultrashort x-ray pulses enable the study of chemical reactions and dynamic change of local electronic densities and structures of gas-phase molecules on the timescale of a few femtoseconds to the attosecond-region. The optimization of coherent and ultrafast x-ray sources of high brilliance over the last decades has led to these new possibilities of imaging dynamic molecular changes and the further development of femtochemistry. Yet these kind of experiments can only be executed at large scale free-electron laser (FEL) facilities. Therefore, users that come to these facilities are often confronted with special challenges, regarding the preparation of their experimental setup.
This report shall give an overview of some of the methods and projects of the *Ultrafast Molecular Imaging*group at the *Center of Free Electron Laser Science* (CFEL) at DESY led by Daniel Rolles. Currently the group is preparing for a beamtime at FLASH (DESY, Hamburg). Therefore this report will present basic techniques, experimental setups and test devices. For ambitious readers the articles [1, 3, 4, 5] are recommended, as well as [11], giving an introduction to femtochemistry.

2 Ultrafast Molecular Imaging

Ultrafast Molecular Imaging in the x-ray region basically deals with the visualization of dynamic changes in molecules electronic structure by studying photons and electrons emitted or scattered by the excited system. Also, there is the possibility to measure the momentum distribution of ionized molecular fragments to gain information.
The technique presented in this report is based on pump-probe experiments on FELs and complemented by experiments with synchrotron radiation sources. The general setup contains the injection of a molecular beam into a ultra-high vacuum (UHV) chamber and the subsequent pumping of the molecules with a femtosecond Ti:Sa laser. The delay of the x-ray pulse is a varying parameter of the experiment and crucial to its outcome, see figure 1.

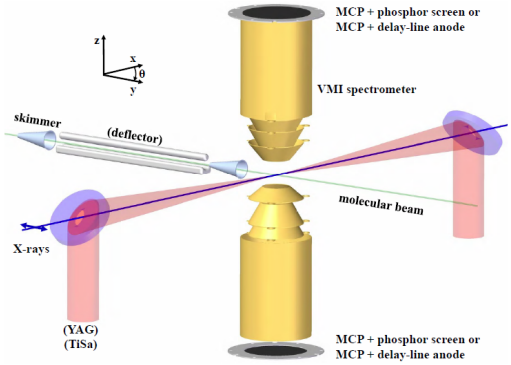


Figure 1: Setup for a pump-probe photoelectron diffraction experiment, [1] p.32

The injected molecules are dissociated by the pump pulse and then further ionized and fragmented by the probe pulse. For their detection, an ion-spectrometer, which covers a solid angle of 4π, is used. The spectrometer consist of several focusing lens providing a reference direction of the electric potential and trajectories of the ions. It is described in more detail in section 2.2. The trajectory of the fragments depends on the molecule's orientation, which is statistically distributed. Therefore the effects of the polarization of the pulses on the dissociation process are not observable. To get rid of this problem, the orientation of the molecular axis is fixed perpendicular to the spectrometers axis by aligning them with a Nd:YAG laser. Laser alignment is based on the induction of an electric dipole through an intense laser field. The interaction of the molecule with the electric field of the alignment laser provides the arrangement of the particles [6, 10].
For the experimental realization of the described challenges, the *Max Planck Advanced Study Group* (ASG) at CFEL developed a multipurpose chamber. It contains a double sided velocity imaging spectrometer (VMI) for simultaneous 4π ion and electron detection and two pnCCD chips to detect scattered x-ray photons.

2.1 CFEL-ASG Multipurpose chamber - CAMP

The *Max Planck Advanced Study Group* (ASG) at CFEL developed a multipurpose chamber, called CAMP, for users of FEL beamlines. It was used for several experiments at LCLS(Linac Coherent Light Source, Stanford University) and is now installed as permanent user endstation at FLASH. The CAMP system consists primarily of the experimental chamber and the supporting frame, see figure 2. The frame enables movements in x-, y- and

z-direction and rotational adjustments about the y- and z-axis.

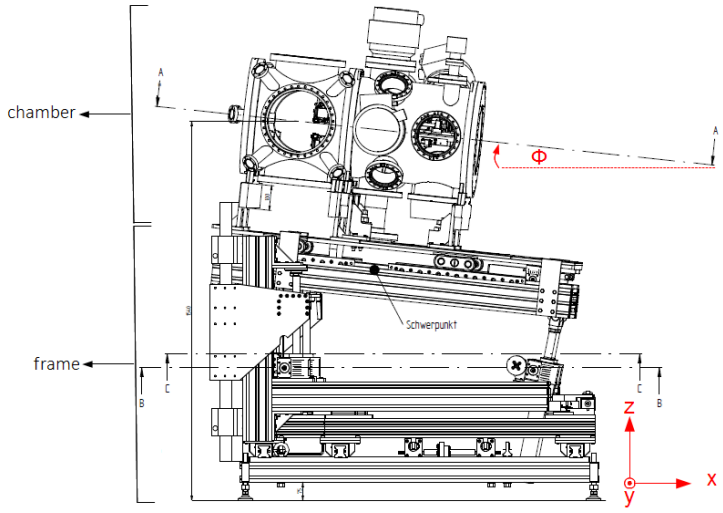


Figure 2: Scheme of CAMP with supporting frame and experimental chamber.

The chamber itself consists of four connected segments [7], see figure 3:

1. Differential pumping stage, the chamber is adapted to the beamline by this segment and holds a pressure of approximately $10^{-8}mbar$ to $10^{-9}mbar$.

2. First main chamber(C1), this segment houses the ion spectrometer and molecule injection device and contains the interaction zone of the FEL and the molecular beam in its center.

3. Second main chamber(C2), this segment houses the first pnCCD which detects photons with a wide scattering angle. The pnCCD consists of two rectangular modules with a central hole to transmit the direct FEL beam which would otherwise damage the CCD.

4. Third main chamber(C3), this segment houses the second pnCCD which detects photons with a low scattering angle. Like the first pnCCD this device consists of two rectangular modules with a central hole.

This experimental system enables momentum resolved detection of electrons and ions over a wide solid angle. Simultaneously, it enables the user to measure scattered or fluorescence photons with the pnCCDs. The measured solid angles are adjustable by the voltage of the focusing lens of the electron/ion

spectrometer, and by the position of the CCDs respectively.

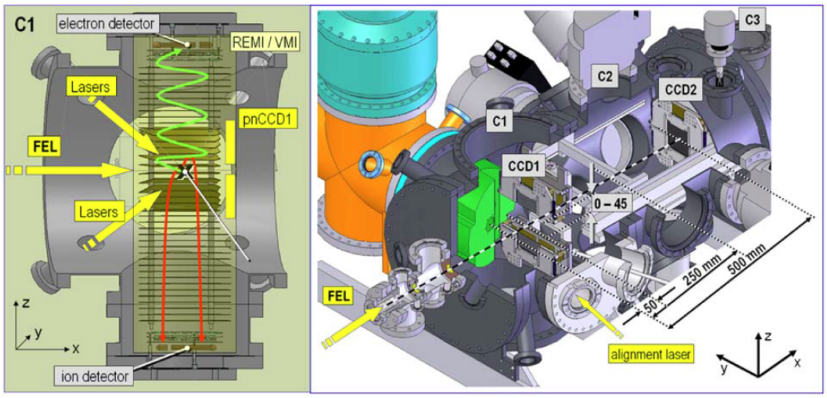


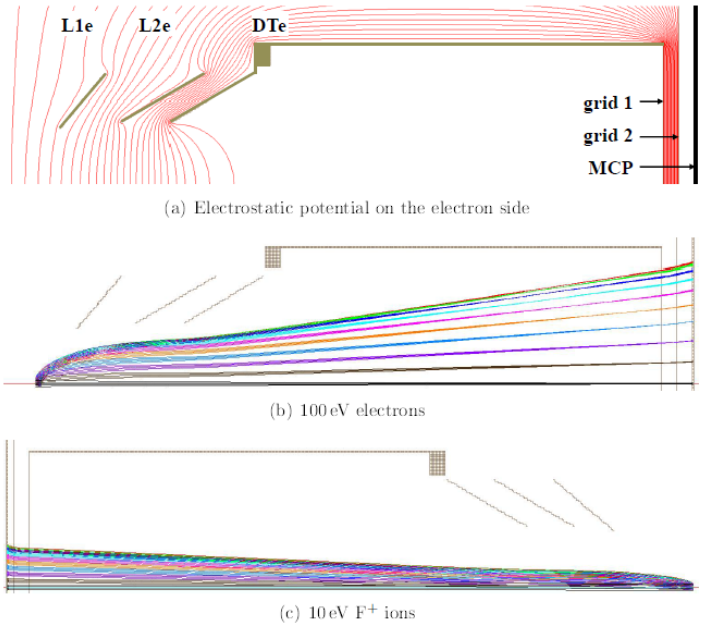
Figure 3: Schematic section trough the CAMP segments. The left scheme shows the first main chamber C1, the right scheme shows a complete system C1 to C3. [7]

The high flexibility of CAMP due to user specific variation of detectors, sample injection, sample holder devices and excitation source, provides the possibility of various experimental setups. For example, for his report, time of flight measurements with an electron gun were realized in order to test the functionality of a VMI and the fragmentation channels of small organic molecules.

2.2 Velocity Map Imaging - VMI

Velocity map imaging (VMI) is a valuable technique for momentum resolved ion and electron measurements with a large acceptance angle during a pump-probe experiment. The detection of charged particles and the reconstruction of their respective momentum is based on a time of flight measurement combined with a two dimensional mapping process, [1, 2] pp.31. The CAMP VMI can be operated either with MCP and phosphor screen detectors as in conventional VMI or with MCP detectors with delay-line-anodes. For the tests using the electron gun setup(see section 3), delay-line-anodes are used. The spectrometer consist of three conically shaped electrodes which are place concentrically on an axis perpendicular to the FEL and molecular beam. These electrostatic lenses accelerate and focus particles due to an inhomogeneous electric field $\vec{E}_{inh}$ on a multichannel plate (MCP), see figure 4. Because of the inhomogeneous electric field, charged particles originating from an extended volume but having the same initial momentum are imaged on the

same radius R in a two dimensional plain.



(a) Electrostatic potential on the electron side

(b) 100 eV electrons

(c) 10 eV F^+ ions

Figure 4: Schematic section through a VMI. a) Electrostatic potential on the electron side of the spectrometer for operation voltages of L1e: 1 kV, L2e: 3 kV, DTe: 7 kV and voltages of opposite polarity on the ion side. (b)+(c)Trajectories of electrons and ions on opposite sides of the VMI spectrometer. Colors correspond to different ejection angles with respect to the spectrometer axis from 0° to 90° with 10° spacing. The five different particles of the same color have different origins between -2 and +2mm offset from the spectrometer axis, [1] p. 37.

This effect corrects blurring phenomena caused by the generation of ions and electrons in a rather wide region of the molecular beam. The radius R is approximately proportional to the square-root of the kinetic energy $\sqrt{E_{kin}}$. Between the lenses and the MCP are two grid-electrodes. The third conical electrode is connected to the first grid forming a closed drift tube region. The MCP consist of a thin plate streaked by fine capillaries forming a lateral amplification device. When an incoming particle hits the surface of a capillary, it generates free electrons which are accelerated by a bias applied to the openings of each tunnel. The accelerated electrons generate additional electrons by hitting the inner surface during their drift through the capillaries. So, the original signal is transformed and amplified by the MCP to an electron pulse and registered by a delay-line behind the MCP, see figure 5.

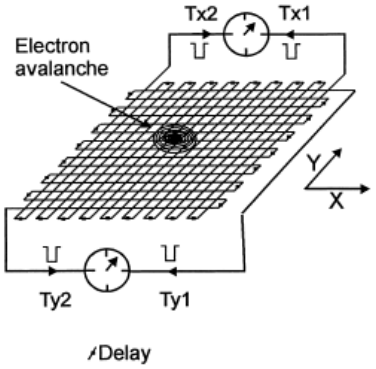


Figure 5: Scheme of a delay-line-anode, [1] p.39

The delay-line consists of two wrapped wires which form a fine mesh. When an electron hits a wire, it generates an electric signal, measured at the wires ends. The position of the triggering particle can be reconstructed by calculating the difference of the runtime of the signal at each end.
For the simultaneous measurement of electrons and positive ions two delay-line detectors are positioned opposite to each other on each end of the double sided VMI.

3 Electron Gun Measurements

To prepare the FEL beamtime experiment, electron gun measurements are performed to test the functionality of detector parts and to study fragmentation of molecules after electron impact ionization.

3.1 Electron Gun

Experiments with a pulsed electron gun (egun) are particularly suited for testing the charged particle spectrometers of the CAMP setup or to observe the single fragmentation channels of new molecules without a FEL source. The setup of an e^-gun is quite similar to an oscilloscope, see figure 6. A filament is heated up by an current I_{fil}, producing free electrons. By increasing the filament current, the amount of charge produced is increased and so is the resulting emission current of the gun. By applying an accelerating voltage U_{ac}, these electrons are brought to energies up to $3keV$. For beam compression, a negative voltage U_W is applied to a metal cone in front of the filament, called the Wehnelt cylinder. The outgoing intensity of the beam can be adjusted by varying U_W.

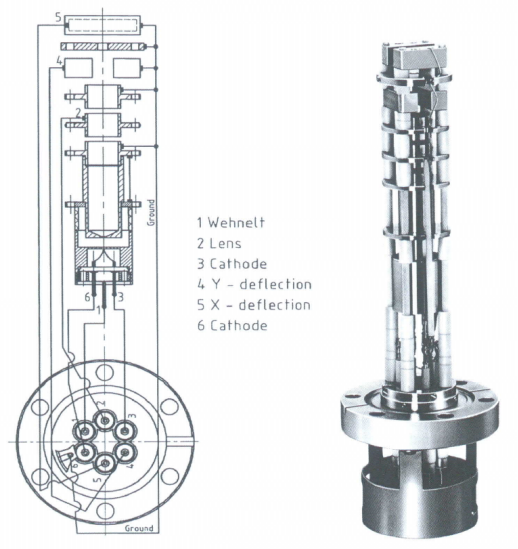


Figure 6: Setup scheme of an electron gun. [9]

The beam is additionally focused by electrostatic lens (2) and positioned by two pairs of deviation plates. For pulsed operation of the egun, the emission current is modulated by applying a pulsed bias to the Wehnelt cylinder.

3.2 Time of flight- ToF

The VMI in the CAMP chamber can be used to study the fragmentation channels of different molecules with an egun instead of an X-ray source. Ions generated by an electron bunch are accelerated by $\vec{a} = \frac{q \cdot \vec{E}}{m}$, whereas m is the particles mass, q its charge, and $\vec{E}$ the applied electric field. Heavy ions therefore need more time than light ones reaching the MCP, the analogue case is holding for the amount of charge. Highly ionized molecules have smaller flight time to the detector than low ionized particles. The presented time of flight(ToF) spectrum was measured with a jet of pure argon. The VMI voltages in this experiment were set to imaging/ToF mode. This provides reasonable results for mere ToF-spectra by covering a wide solid angle. The experiments are based on the detection of positive ions produced by the excitation of the electron beam and focused by the upper lenses. The applied spectrometer voltages are shown in table 1.

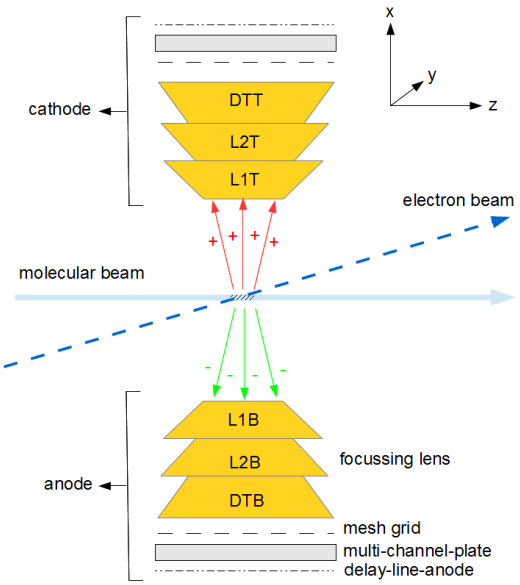


Figure 7: Schematic setup for time of flight measurements.

The experiments with the argon jet were performed at a pressure of approximately $9 \cdot 10^{-8} mbar$ in the C1 main chamber and an injection pressure of $1,5 bar$. The electron beam energy was $2 keV$ with a Wehnelt bias of $61,2 V$.

L1B(L1T)	L2B(L2T)	DBT(DTT)	1. grid	2. grid
(-)200 V	(-)500 V	(-)615 V	-2850 V	-2800 V

Table 1: VMI parameters during ToF experiments, nomenclature according to figure 7. The first grid is also designated as mesh b top as the second one is designated as DET T.

Since the time of flight is proportional to the squareroot of the mass-charge ratio of the particle [1], the qualification and calibration of the spectra is possible by a 'educated guessing'. First, several significant peaks in a ToF-spectrum have to be identified for their mass and charge characteristics. Then the respective flight times T in dependence of their suspected mass to charge ratios (m/q) are plotted. After that, the plotted points are fitted by a linear function of the form $T = \alpha \cdot \sqrt{m/q} + \beta$, see figure 8. Now it is possible to extrapolate the (m/q) value for any other significant peak in the original spectrum.

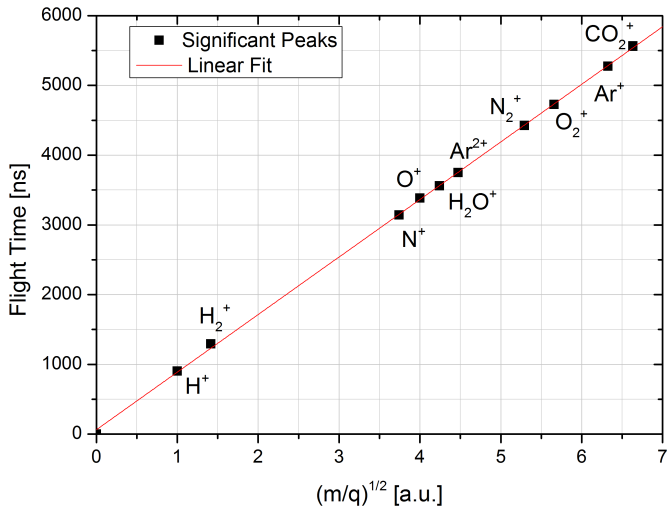


Figure 8: Mass-charge-ratio plotted to the time of flight.

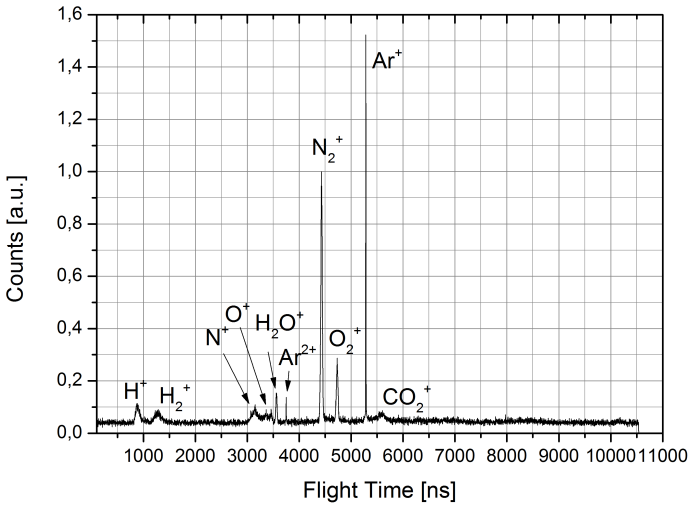


Figure 9: Time of flight spectrum of Argon. High background signal due to oxygen, nitrogen and water in the chamber.

It can be clearly seen in figure 9 that the amount of rest gases like oxygen, nitrogen and water vapor in the chamber is not negligible and causes a significant background signal. ToF spectra of noble gases as argon are often

used for calibration of the the spectrometer due to their defined and well known ionization states.
There was also the attempt to measure a ToF of tetrahydrofuran (THF, C_4H_8O). For this experiment a bubbler filled with THF was used to create a jet. Argon and helium served as carrier gases. The study of the fragmentation of THF is a far more complicated task, since unlike argon, there is a large variety of channels for the molecule to disintegrate [8]. THF is a molecule with an analogue structure to deoxyribose ($C_5H_{10}O_4$) as it is a constituent of DNA or RNA polynucleotide chains, see figure 10.

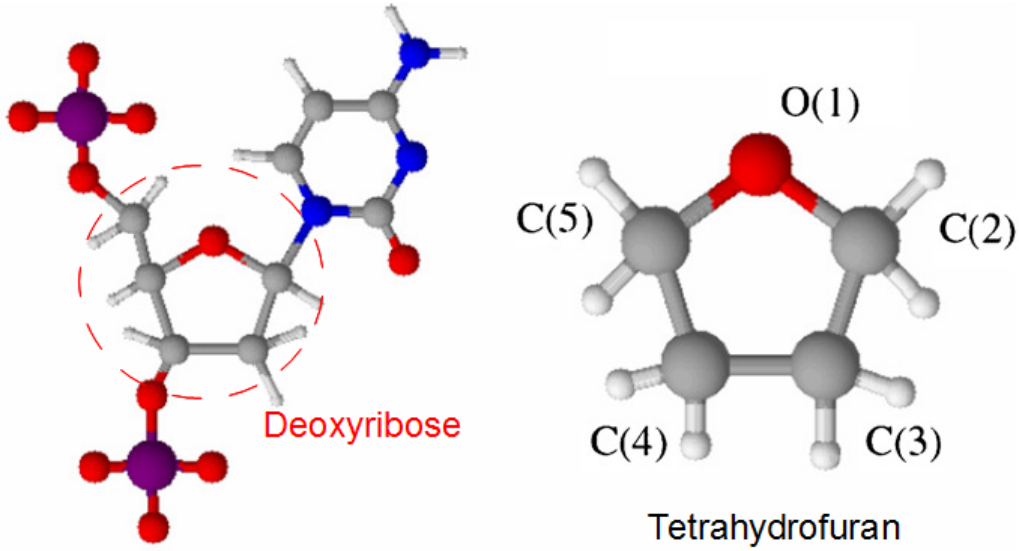


Figure 10: Schematic diagrams of DNA fragment (left), containing deoxyribose and a tetrahydrofuran molecule(right). Labeling of atoms is shown for the tetrahydrofuran molecule. Color code: the carbon atom is gray, oxygen atom red, hydrogen atom light gray, phosphorus atom purple and nitrogen atom blue. [8]

Unfortunately, it was not possible to visualize the ions and fragments THF in an ToF .So far, strong background signal due to water, oxygen and nytrogen and a poor SNR prevented a successful conclusion of the experiment.

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