

Contents and objectives of this video



- XFEL science
 - Time resolution
 - Pump-probe
 - High intensity
 - Extreme states of matter

Hi and welcome back to the last video of the third and final section of week four of this course, Synchrotrons and X-ray Free-electron Lasers: Techniques and Applications. In this section, I will show four examples that have emerged in the first decade of XFEL science. This can be divided into the two properties of XFELs that most interest. First, time for resolution in classical pump-probe experiments, and second, high intensities, inducing extreme states of matter.

Notes

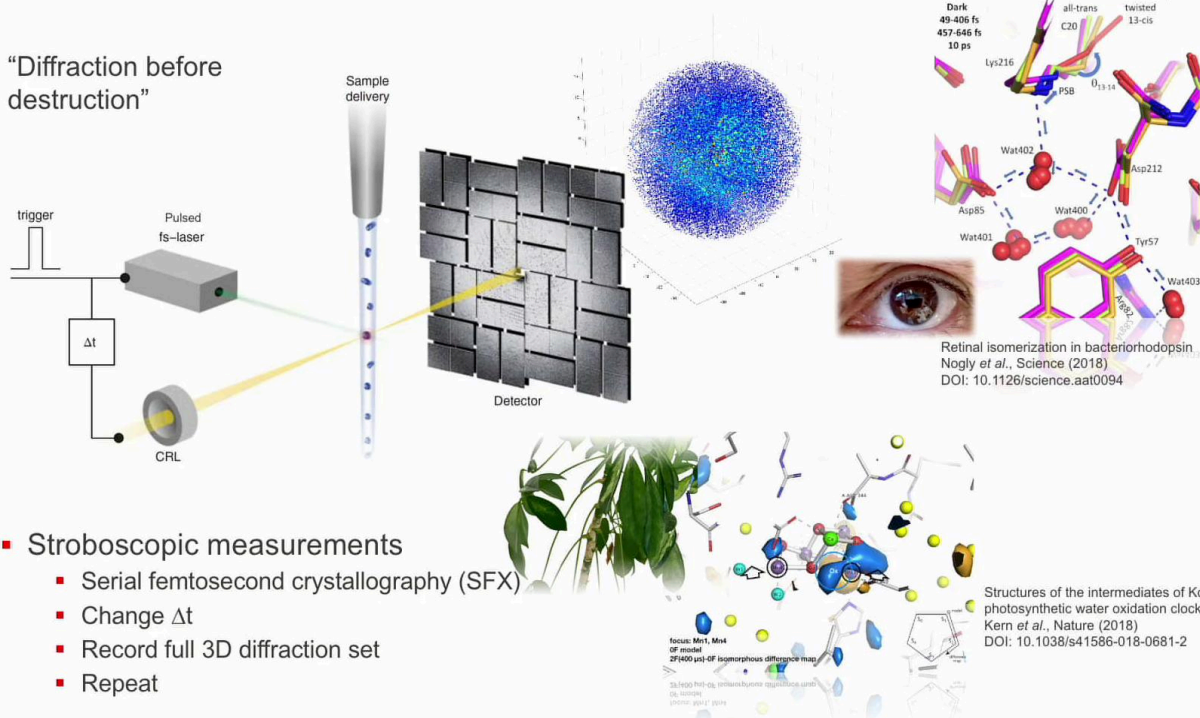
Summary



0m 05s

Biochemistry

"Diffraction before destruction"



- Stroboscopic measurements
 - Serial femtosecond crystallography (SFX)
 - Change Δt
 - Record full 3D diffraction set
 - Repeat

We begin with one of the first major goals in XFEL science to be pursued as soon as the LCLS came online in Menlo Park, California, namely, time-resolved femtosecond crystallography of important biochemical processes. A typical experiment involves a collection of micron-sized crystals being delivered to the cross point between a pump femtosecond laser and XFEL radiation. The laser induces a photochemical reaction, which is probed by the XFEL after a time delay, Δt , which is increased from pump only a few femtoseconds, up to, perhaps, a nanosecond. And much larger delays than this, it becomes more efficient to use synchrotron radiation. In most instances, the diffraction pattern produced by scattering of the XFEL radiation, by the small protein crystals, will contain a random subset of all the possible diffraction peaks that can be accessed due to the uncontrolled and random orientation of any one crystal in the X-ray beam. Consequently, many such patterns need to be recorded, typically measured in the tens or hundreds of thousands in order to fill the entire pattern in a statistically reliable manner. And this is the case for each individual time delay.

Notes

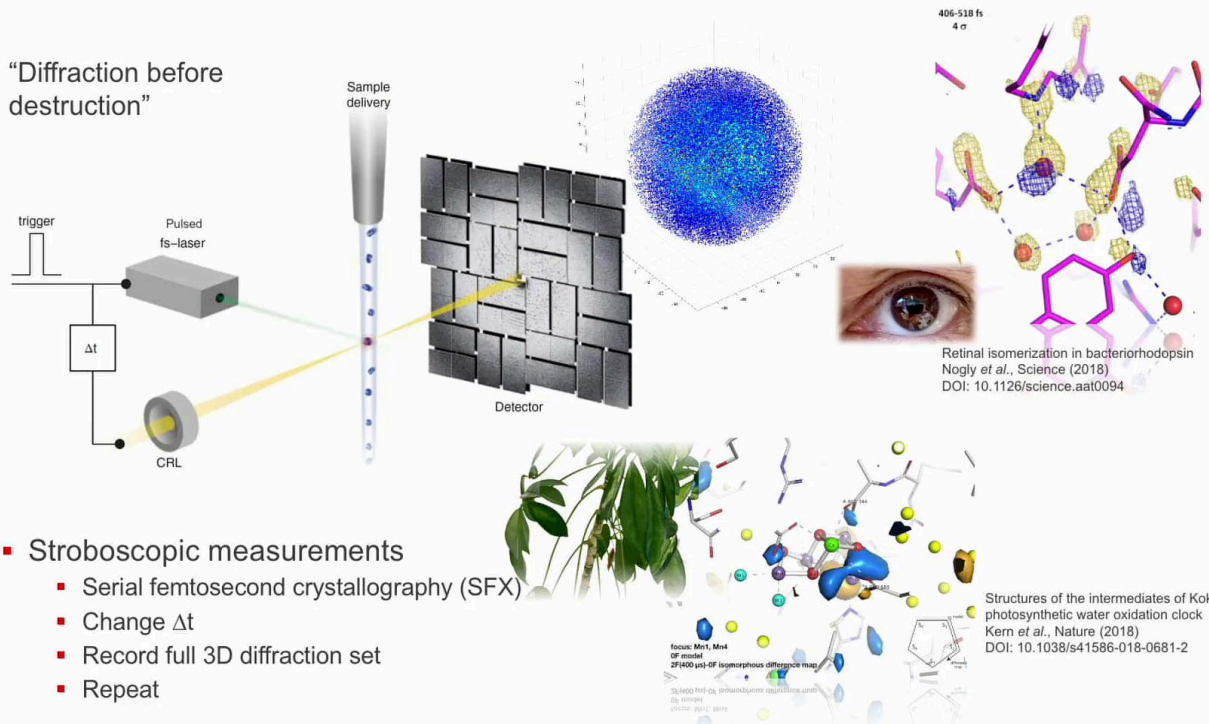
Summary



0m 38s

Biochemistry

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Hence, one can record several million diffraction patterns before a time-resolved measurement is complete, which can take several days to complete and result in petabytes of data. And this is before any of the data has even been analysed. Two high-profile examples of such experiments are shown here. Top right is the process of retinal isomerization in bacteriorhodopsin, showing the reconfiguration of the light sensitive region in the first ten picoseconds. The example below this investigates intermediate structures of Kok's synthetic water oxidation clock.

Notes

Summary



2m 08s

Single-particle imaging

Advantages

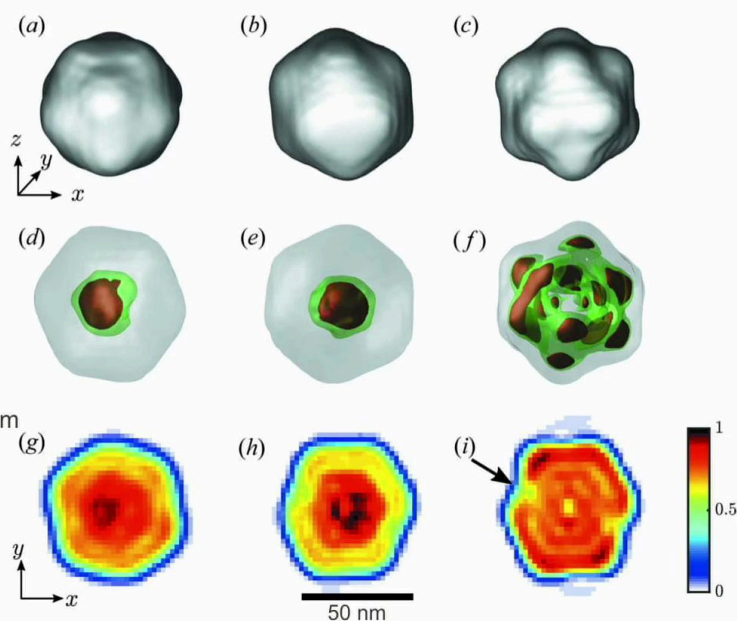
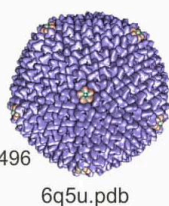
- Room-temperature measurements
- No radiation damage
- No crystallization required
- Dynamics studies possible

This study

- PR772 bacteriophage virus
 - ca. 70 nm diameter
- LCLS, AMO instrument
- $E = 1.5 \text{ keV}$ (0.775 nm)
- Ultimate possible resolution 0.3875 nm
- Obtained resolution ca. 5 nm

c.f. cryoEM:

- 2.75 Å
- H.K.N. Reddy *et al.* (2019)
- DOI: 10.7554/eLife.48496



Single-particle imaging without symmetry constraints at an X-ray free-electron laser
M. Rose *et al.*, IUCrJ (2018)
DOI: 10.1107/S205225251801120X

The second example, also from the world of molecular biology, takes advantage more of the high intensities offered by XFELs than their time resolution. Single-nano scale particles scatter much too weakly for them to be observed using synchrotron light. However, the hugely greater transient peak flux offered by XFELs make such experiments possible. The principle behind such experiments is similar to that given in the previous example, but without the pump source and variable time delay. Being single particles, the scattering pattern does not contain discrete Bragg Maxima associated with crystals, but instead a diffused-pattern that extends out to, approximately, plus or minus 10 degrees. Advantages of this approach are, one, the experiment can be carried out at room temperature, and two, no radiation damage is observed, as the scattering pattern is generated before the particles explode. Cryo-cooling will not change its end fate. Thirdly, no crystallisation is required in contrast to serial femtosecond crystallography. And lastly, although this was not performed in the example shown, dynamic studies can also be performed.

Notes

Summary



2m 50s

Single-particle imaging

Advantages

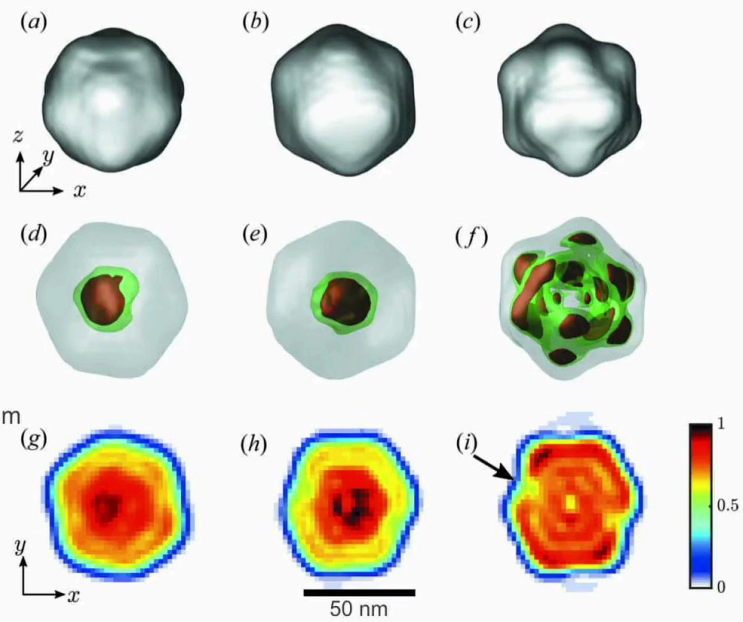
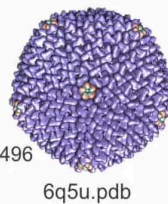
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This study was performed on the PR772 bacteriophage virus, a structure showing an icosahedral symmetry with a diameter of approximately 17 nanometres. It was irradiated with 1.5 keV photons, which have a wavelength of 7.75 angstroms. In theory, the ultimate possible resolution of such an experiment is half the size of the wavelength, that is, 3.875 angstroms obtained in the exact backscattering direction of 2 Theta equals 180 degrees. Unfortunately, the scattering pattern drops off extremely rapidly with the angle of detection away from the forward direction axis. And in fact, the obtained resolution was only about 50 angstroms. This result should be contrasted with the cryo-electron microscopy study of Reddy *et al.* who were able to obtain an approximately 20 times superior resolution. The use of XFEL radiation is, therefore, only warranted if issues related to cryo-cooling are evident, or dynamic studies in the femtosecond to microsecond timescale are required.

Notes

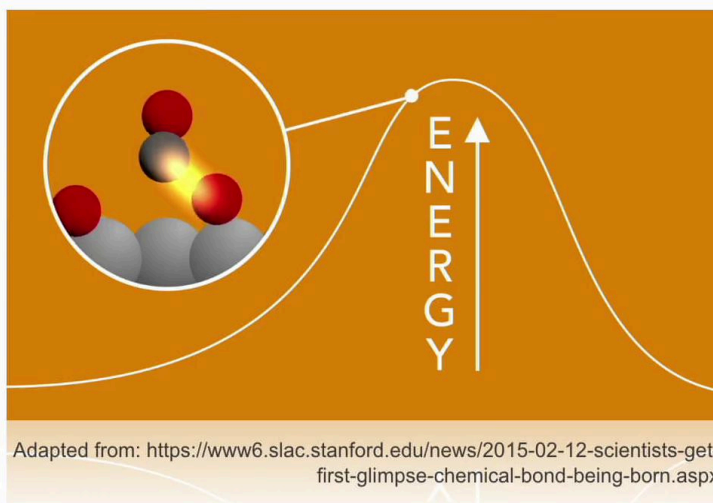
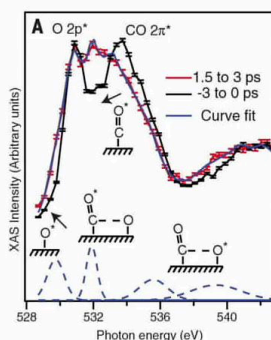
Summary



4m 07s

Chemical bond breaking and formation

- Chemical bond dynamics
 - Core goal of much of chemistry
 - Nonequilibrium transient states
- This study
 - Neutralization of CO on automotive Ru-catalyst
 - LCLS/SXR beamline
 - Oxygen-XANES



H. Öström *et al.*, Science (2015)
DOI: 10.1126/science.1261747

One of the strongest justifications for building a billion-dollar price tag XFEL is its use in time resolve chemistry, and the elucidation of nonequilibrium transient states. Insights gained here might lead to more efficient catalytic systems, enhanced environmental sequestration of harmful gaseous species, and superior batteries and fuel cells, to name just three examples. Typically, such experiments require both the high transient power time resolution of XFELs. The example shown here is of the atomic scale and femtosecond-resolved movie of the neutralisation of CO on Ruthenium catalysts in the automotive industry. The orientation of the component oxygen and carbon-containing species could be determined by interpreting Oxygen-XANES spectra at different time delays, resulting in the formation of CO₂. We will discuss XANES in more detail in the sister course.

Notes

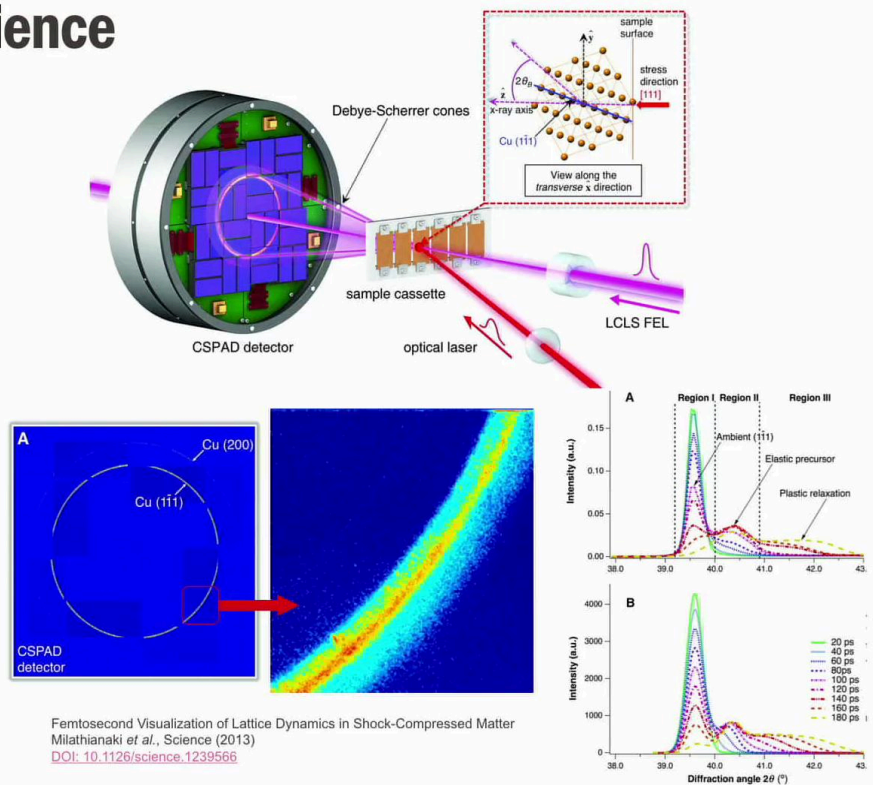
Summary



5m 23s

High-pressure science

- Transition from elastic to plastic deformations
 - Laser shock-compression of copper
 - Up to 73 GPa
- Few ps timescale
- < 1 μm resolution
- Relevant to
 - Astrophysics
 - Geophysics
 - Fission-enclosure materials



The last example is in high-pressure science. Matter under high pressure and/or high temperature is still only partially understood. In the example here, copper is laser shock-compressed to pressures exceeding 70 GPa. This level of pressure becomes relevant for many astrophysical and geophysical processes. For example, the pressure of the Earth's inner core is thought to be only a factor of 5 higher than this. Diamond synthesis is thought to occur at only 10-20 GPa. See also the Wikipedia link given here, which lists relevant pressures across many orders of magnitude. In the movie shown here, the Debye-Scherrer powder diffraction ring of copper is recorded up to 200 picoseconds.

Notes

Summary



High-pressure science



See also: Liquid explosions induced by X-ray laser pulses
Stan *et al.*, Nature (2016)
DOI: [10.1038/nphys3779](https://doi.org/10.1038/nphys3779)
and <https://www.youtube.com/watch?v=v5bH01qNN0Y>

The pressure exerted by the deposited energy of samples in XFELs can have unexpected and undesired consequences.

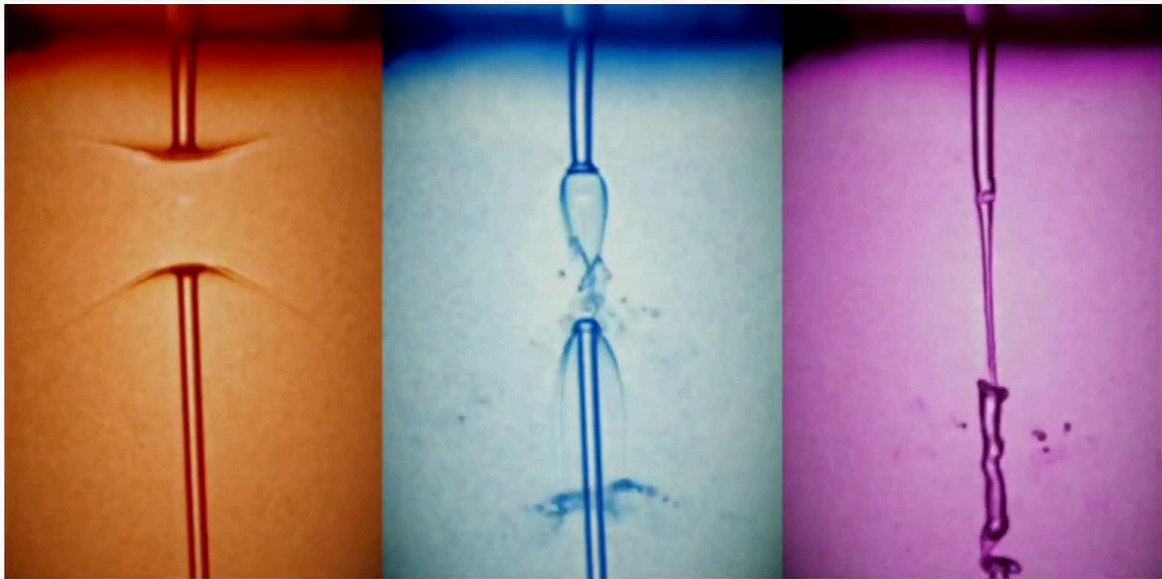
Notes

Summary



7m 20s

High-pressure science



See also: Liquid explosions induced by X-ray laser pulses
Stan *et al.*, Nature (2016)
DOI: [10.1038/nphys3779](https://doi.org/10.1038/nphys3779)
and <https://www.youtube.com/watch?v=v5bH01qNN0Y>

A highly relevant example is shown here where buying narrow water jets containing protein crystals in serial femtosecond crystallography experiments can be completely obliterated by absorption of only a very small fraction of the incident XFEL radiation. This requires time on the scale of milliseconds to heal, thus, limiting the repetition rate of such experiments.

Notes

Summary



7m 36s

High-pressure science



See also: Liquid explosions induced by X-ray laser pulses
Stan *et al.*, Nature (2016)
DOI: [10.1038/nphys3779](https://doi.org/10.1038/nphys3779)
and <https://www.youtube.com/watch?v=v5bH01qNN0Y>

But water is cheap. Even if the protein crystals contained in it can be considerably more expensive. Note, for instance, that single crystals of novel materials with possible applications in future electronics can be extremely expensive, and careful considerations must be made to ensure that they are not destroyed in XFEL experiments.

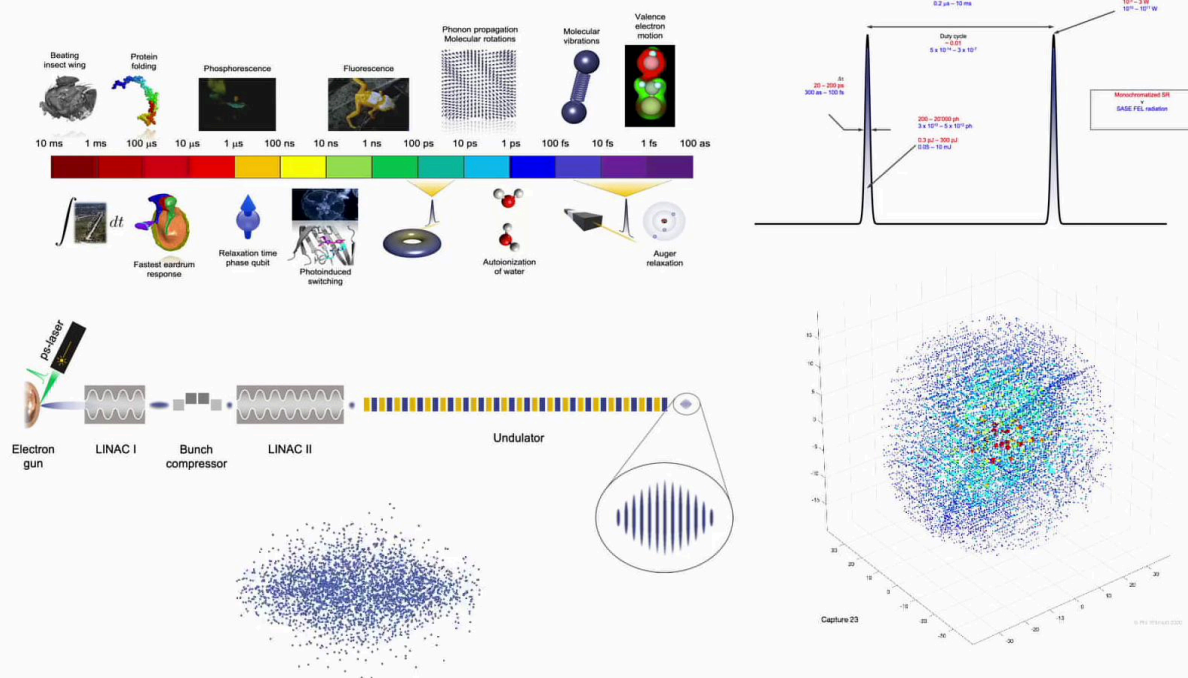
Notes

Summary



7m 55s

Summary of this section



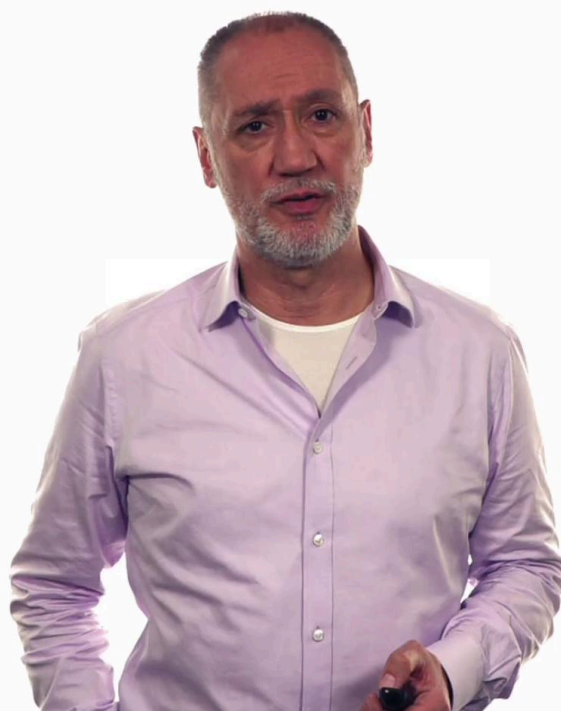
This section was concerned with an overview of XFELs. We began by considering different orders of magnitudes of processes that occur in the natural world and by comparing the properties of XFEL and synchrotron radiation. In what manner, the former can be useful in time resolved experiments. We, then, took a brief tour of the architecture of XFELs, and then, looked in some detail as to how SASE induces the formation of microbunches. We finished this section by looking at some scientific highlights and XFEL techniques in the decade since their first use in 2009.

Notes

Summary



Next week...



Next week, and indeed the week after, we turn to X-ray optics and beamline instrumentation. In the first of these two weeks, we consider the heart of the beamline, namely, mirrors and monochromators.

Notes

Summary



8m 57s