Workshop on the scientific opportunities of a THz FEL in Sweden

Organized by the Stockholm-Uppsala FEL centre

November 24-25, 2014

at AlbaNova University Center, Stockholm University

Peter Salén, May 2015
1. Introduction

The workshop was held on the 24th and 25th of November 2014 at AlbaNova University Center in Stockholm. The main goals of the workshop can be summarized as follows:

1. Obtain an overview of current THz research in Sweden, with a non-exclusive emphasis on those research activities that use THz radiation for spectroscopic and/or imaging purposes.
2. Establish a potential user base for a prospective THz FEL facility.
3. Discuss possible modifications to our preliminary design for a THz FEL facility such as to accommodate the largest user community possible.

Registration for the workshop was free of charge and the invited speakers were reimbursed for travel and lodging expenses in an attempt to attract as many scientists as possible. A workshop dinner was organized on the evening of Monday the 24th of November.

Forty-five people registered for the conference. Forty-three of them were associated with Swedish universities while the remaining two originated from Germany and Ukraine, respectively. The distribution of the ‘Swedish’ participants over their home institutions is given in Table 1. It can be seen that scientists from 9 different Swedish universities took part in the workshop, with an excellent geographical spread over the country: ‘from Lund to Luleå’.

The workshop featured 19 invited presentations of either 20 or 40 minutes duration, see program in the appendix. Some of the invited speakers suggested ideas for future THz research projects rather than presenting actual results. It is not unreasonable to expect that the number of scientists that exploit the properties of THz radiation in their research will rise sharply in the years to come, in particular if proper THz light sources will be made available to them. All participants that have no access to our internal KTH-SU-UU FEL centre Indico web pages was sent the 19 workshop presentations in pdf format on an USB memory stick.
Table 1. Distribution of the ‘Swedish’ participants over their home institutions.

<table>
<thead>
<tr>
<th>Institution</th>
<th>Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stockholm University</td>
<td>14</td>
</tr>
<tr>
<td>Uppsala University</td>
<td>9</td>
</tr>
<tr>
<td>Gothenburg University</td>
<td>7</td>
</tr>
<tr>
<td>Lund University / MAX IV</td>
<td>3</td>
</tr>
<tr>
<td>Chalmers Technical University</td>
<td>3</td>
</tr>
<tr>
<td>KTH</td>
<td>2</td>
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<tr>
<td>Luleå University of Technology</td>
<td>2</td>
</tr>
<tr>
<td>Linköping University</td>
<td>2</td>
</tr>
<tr>
<td>Mid Sweden University</td>
<td>1</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>43</strong></td>
</tr>
</tbody>
</table>
2. Executive summary

The initial three presentations of the workshop described the FREIA laboratory (a likely location of the Swedish THz FEL), the new IR FEL at Fritz Haber Institute (FHI) in Berlin, and the proposed Swedish THz FEL. The FHI FEL is, similarly to the envisioned Swedish FEL, based on superconducting accelerator technology, which provides a high average output power. Another similarity is the use of a cavity mirrors surrounding the undulator in both designs in order to build up the laser intensity. This is a proven design which puts less demands on the quality of the electron bunches compared with a super-radiant FEL where the THz pulses only pass through the undulator once and which requires short electron packages. On the other hand the super-radiant source is more flexible with respect to the repetition rate. The FHI FEL is constructed with a mid-IR undulator but includes a THz FEL as a possible upgrade, while the Swedish design combines the THz undulator with an X-ray source.

The following talks presented the THz activities at various Swedish research groups and their interest in using the proposed THz FEL. It revealed that a broad range of THz research is performed in the country and that there is a strong interest in such a light source.

Vasyl Yatsyna from Gothenburg University presented gas-phase studies conducted at the IR-FEL FELIX in Nijmegen. He showed that measurements of IR/THz frequency vibrations are useful for molecular structure determination and exemplified with the experimental resolution of distinct peptide conformers.

Serguei Cherednichenko described the THz projects at the Institute of Microtechnology and Nanoscience (MC2) which belongs to Chalmers University of Technology. These projects include development of THz sources, detectors, and electronics. They would be interested in using a THz FEL for verification of their THz multiplier sources, and for material analysis.

Carlito Ponseca from Lund University presented studies of transport properties of solar cell materials, with focus on the oregano metal halide perovskite, using time-resolved THz spectroscopy. This work sheds light on the fundamental photophysical processes in these materials which is crucial for the development of solar cells.

Stefano Bonetti is affiliated with Stockholm University but has been working at SLAC using both laser-, and accelerator-based single-cycle THz sources. He gave an overview of his work where single-wave THz pulses have been applied to e.g. the investigation of control of magnetism and phase transitions. These measurements were also combined with X-ray diffraction probing.

A theoretical view on spin and magnetization dynamics in the THz regime was presented by Corina Etz (Uppsala University, Luleå Technical University). At Uppsala they have developed a simulation tool for atomistic spin dynamics that provides static and dynamic information of materials which can be directly compared with experiments. She exemplified with simulated spin-wave spectra of a magnetic material that displayed good agreement with experimental data.
At Linköping University, Vanya Darakchieva is the head of a group that plans to build a THz magneto ellipsometer which will be the core of a new facility for THz materials preparation and analysis. The THz magneto ellipsometry allows for measurements of electronic transport properties, in e.g. multilayered structures, and can be used for characterization and feedback at materials fabrication, such as of graphen, which will lead to developments in THz electronics. Vanya suggested that a THz ellipsometer could be a potential instrument for a THz FEL.

The microwave group at Uppsala University has a vast experience with microwaves and mm-waves for imaging and bio-medical applications and is involved in several EU and national projects. Dragos Dancila presented their work which includes bacterial recognition via THz time-domain spectroscopy (TDS) and the development of a mm-wave probe for cancer diagnosis. The microwave group could contribute to a THz FEL project with equipment, expertise, and preliminary measurements with THz-TDS.

Dag Hanstorp from Gothenburg University described experiments where strong laser fields were employed to induce orbital alignment in atoms by electron photodetachment of negative ions. They have demonstrated the possibility to initiate and monitor electron motion in neutral atoms which can be useful for the control of chemical reactions.

Gergely Katona leads a group at Gothenburg University that studies biological molecules using X-rays and THz radiation. Here he talked about X-ray crystallography experiments on lysozyme that revealed long lived THz-induced vibrational motions which are likely to be related to a Fröhlich process where vibrational modes condensate into a long lived collective mode. He also discussed the role of THz radiation in living organisms and life-science experiments with a THz FEL and X-ray source.

Olof Karis who is the head of the molecular and condensed matter physics department at Uppsala University described the relevance of the GHz-THz frequency range for studies of solid state samples and specifically magnetization dynamics. He exemplified by presenting several experiments using THz pulses for pumping and probing.

Alexander Soldatov from Luleå University of Technology presented their investigations of carbon nanostructures at high pressures. They study e.g. phase transitions and structural integrity of these materials as a function of pressure using tools such as Raman and FTIR spectroscopy, and microscopy. He proposed broad band THz spectroscopy as a useful complement to these experiments.

Richard Neutze who is affiliated with Gothenburg University described measurements of ultrafast protein structural changes using time-resolved wide-angle X-ray scattering. He further suggested related THz pump-probe experiments where the THz pulses could be used for driving protein dynamics or probing its motion.

Anders Nilsson from Stockholm University discussed how THz radiation could be applied to surface science and studies of water. Short strong-field THz pulses could for example be used
to exert control of molecules on a surface. Furthermore, longer pulse ranges for THz induced surface processes could be investigated with the proposed THz FEL facility. He proposed that the light source would also be useful for measurements of slow time-scale motions in water.

Stacey Sörensen from Lund University talked about applications of the THz FEL to gas-phase and cluster photochemical reactions. She presented several examples of experiments suitable for the envisioned light source, such as the THz excitation of ring vibrational modes that could be probed with X-rays, and the study of the THz vibrational modes of water nanoclusters coupled to complexes by pump-probe measurements.

The final presentation was given by Christer Fröjdh who described the research performed on X-ray detectors and their applications at the Mid Sweden University. He specifically discussed spectral X-ray imaging which is a powerful method for identifying materials in a complex object and proposed that the combination of THz with this technique should be further explored.

The workshop also included a discussion session lead by Peter van der Meulen from Stockholm University. Here the participants were asked to select their preferred choice between three possible output characteristics of the proposed THz FEL, shown in Table 2.

<table>
<thead>
<tr>
<th></th>
<th>Short-pulse</th>
<th>Standard</th>
<th>High-resolution</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Frequency</strong></td>
<td>1 THz</td>
<td>1 THz</td>
<td>1 THz</td>
</tr>
<tr>
<td><strong>Repetition rate</strong></td>
<td>1-100 kHz</td>
<td>176 MHz</td>
<td>176 MHz</td>
</tr>
<tr>
<td><strong>Pulse energy</strong></td>
<td>200 µJ</td>
<td>20 µJ</td>
<td>1 µJ</td>
</tr>
<tr>
<td><strong>Pulse length</strong></td>
<td>5-10 ps</td>
<td>40 ps</td>
<td>long</td>
</tr>
<tr>
<td><strong>Bandwidth</strong></td>
<td>$\Delta \lambda / \lambda = 5 \times 10^{-2}$</td>
<td>$\Delta \lambda / \lambda = 10^{-2}$</td>
<td>$\Delta \lambda / \lambda = 10^{-4}$</td>
</tr>
</tbody>
</table>

A majority of the participants agreed that the short-pulse option would be the most desirable because of the short pulse length and lower repetition rate which are more suited for pump-probe experiments. The lower repetition rate of 1-100 kHz could be achieved by extracting the THz pulses with a mirror that is only reflecting when exposed to an IR pulse, although this needs to be investigated more. Further studies are also necessary to confirm the pulse energy and duration, and thus this option creates some additional risk compared to the other choices. However, the remaining options were considered interesting as well. For example, the standard version is already unique because of its high power which makes it attractive for
action spectroscopy experiments. A strong interest was also expressed for the possibility of combining THz and X-rays in pump-probe experiments.

In the discussion session the topic of a THz platform was also brought up. It was pointed out that by uniting the THz electronics and FEL community a large THz group exists in Sweden.
3. Summary of presentations

"The FREIA laboratory and its future developments” – Tord Ekelöf (Uppsala University)

Tord Ekelöf informed about the FREIA (Facility for REsearch Instrumentation and Accelerator development) laboratory located at Ångströmlaboratoriet, Uppsala University, which was constructed to develop and test accelerator components and was inaugurated in June 2013. Presently FREIA is involved in its first project which is to develop the RF-system for the linear proton accelerator that will be used at the European Spallation Source (ESS) in Lund for generation of its neutron flux. They are also testing the superconducting high-power spoke cavities for ESS. The first contract period (2012-2015) was financed by ESS, the government, KAW and Uppsala University, and allowed most of the basic investments for the ESS test and development program to be made. A new collaboration contract with ESS for 2016-2018 is being discussed. As from 2019 one or several new projects can be undertaken by FREIA. One such project is the construction of a superconducting THz FEL in the FREIA building. The build-up of competence and equipment at FREIA is of vital importance for such a future project.

The layout of FREIA is shown in Fig. 1. The cryogenics were commissioned in March 2014 and consist of a liquefier that delivers 140 l/h liquid helium to a 2000 l dewar. The dewar has 3 outlets for connection to experiments and one for filling mobile dewars. A 20,000 l liquid nitrogen dewar has been installed which provides pre-cooling for the liquefier. The helium gas recovery system includes a 100 m³ gas bag.

Fig. 1. Layout of FREIA.
A Horizontal Cryostat designed at FREIA, called HNOSS, was delivered in August 2014 and will be integrated in the cryogenic loop. It will be used for testing of superconducting accelerator cavities, magnets and more [1,2].

Of the three concrete bunkers, the largest will have inner dimensions 10.4 m (length) x 4 m (width) x 4.8 m (height). It will house the HNOSS. The surrounding protective walls will bring the ionizing radiation down to < 1 µSv/h outside the bunker. Radiation safety authorization for operation was received in Jan 2014.

The double spoke cavities housed inside cryomodules to be used at the ESS accelerator are developed at IPN Orsay. After initial testing there, one cavity will be brought to FREIA at the end of 2014 for further tests in HNOSS. First at low power to verify the Orsay measurements, and then at full power for verification, before ordering all 26 cavities.

An RF distribution system will connect the RF-power stations (including 2 tetrode, 1 solid state amplifier) with the HNOSS and the cryo modules. Both coaxial and waveguide lines will be used for the RF distribution. The former is smaller and should be sufficient for the required 400 kW peak power, but both will be tested. FREIA is also developing control systems that will be compatible with the ESS standards.

“The new IR FEL facility at the Fritz-Haber institute in Berlin” – Wieland Schöllkopf (Fritz-Haber-Institut, Berlin)

Wieland Schöllkopf was invited to give an “inspirational talk” about their newly constructed IR FEL at the Fritz-Haber institute (FHI) in Berlin. The basic design [3,4] is shown in Fig. 2 and includes two separate undulator lines, both with the undulators placed between cavity
mirrors. The Mid-infrared (MIR) FEL performs in the wavelength range of 4-50 μm and started user operation in 2013, while the Far-infrared (FIR)/THz FEL, which is still only projected as a possible upgrade, will provide access to the wavelength region of 40-500 μm. A normal conducting S-band linac accelerates the electrons generated by a gridded thermionic gun to energies of 15-50 MeV. The electron bunches can be distributed to either the diagnostic beam line or the undulator lines. Table 3 summarizes the parameters of the electron beam and the output of the MIR-FEL.

Table 3. Electron beam and MIR-FEL output parameters.

<table>
<thead>
<tr>
<th>Electron beam parameters</th>
<th>Output MIR-FEL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron energy</td>
<td>15-50 MeV</td>
</tr>
<tr>
<td>Micro-pulse energy</td>
<td>10-20 μJ</td>
</tr>
<tr>
<td>RF frequency</td>
<td>3 GHz</td>
</tr>
<tr>
<td>Micro-pulse length</td>
<td>0.3-&gt;5 ps</td>
</tr>
<tr>
<td>Bunch repetition rate</td>
<td>1 GHz</td>
</tr>
<tr>
<td>Macro-pulse energy</td>
<td>~100 mJ</td>
</tr>
<tr>
<td>Bunch charge</td>
<td>&gt;200 pC</td>
</tr>
<tr>
<td>Macro-pulse length</td>
<td>&gt; 10 μs</td>
</tr>
<tr>
<td>Bunch length</td>
<td>1-5 ps</td>
</tr>
<tr>
<td>FT-lim. band width</td>
<td>0.3-5%</td>
</tr>
<tr>
<td>Macro-bunch length</td>
<td>8 μs / 15 μs</td>
</tr>
<tr>
<td>Macro-bunch repetition rate</td>
<td>10 Hz</td>
</tr>
</tbody>
</table>

Although the FIR FEL is not installed yet, it has been designed and the specification of both the MIR and FIR undulator is summarized in Table 4. The 2 m long MIR undulator contains 50 periods with a 40 mm period length and the undulator gap can be adjusted corresponding to rms-K values between 0.5-1.6. The outcoupling mirror of the cavity can be switched between mirrors with different hole diameters, between 0.75 mm and 3.5 mm, in order to choose the most suitable hole size for the wavelength region of interest. The cavity mirrors are concave and create a Rayleigh length for the radiation in the cavity of about 1 m. A wave guide is not utilized for the MIR cavity but it will be necessary for the FIR FEL due to the higher diffraction at longer wavelengths.
Table 4. Specifications of the MIR and FIR undulators at the FHI FEL.

<table>
<thead>
<tr>
<th>Undulator</th>
<th>MIR</th>
<th>FIR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type</td>
<td>Planar hybrid</td>
<td>Planar hybrid or PPM</td>
</tr>
<tr>
<td>Material</td>
<td>NdFeB</td>
<td>NdFeB or SmCo</td>
</tr>
<tr>
<td>Period (mm)</td>
<td>40</td>
<td>110</td>
</tr>
<tr>
<td>Number of periods</td>
<td>50</td>
<td>40</td>
</tr>
<tr>
<td>Length (m)</td>
<td>2.0</td>
<td>4.4</td>
</tr>
<tr>
<td>K_{rms}</td>
<td>0.5-1.6</td>
<td>1.0-3.0</td>
</tr>
<tr>
<td>Cavity length</td>
<td>5.4</td>
<td>7.2</td>
</tr>
</tbody>
</table>

The cavity length can be adjusted with a translation stage, which determines the gain, but is also related to the time structure and band width of the IR pulses. In order to measure the micro-pulse time structure they use an autocorrelator setup. The autocorrelator measurements show a small FEL gain and generation of short IR pulses with FWHM duration of about 0.4 ps at a small cavity detuning of -3 µm. With increasing cavity detuning of the cavity length relative to the condition of equal electron bunch repetition rate and laser pulse roundtrip time, the pulse length increases and at a detuning of -50 µm the pulse length reaches a maximum of several picoseconds. The large variation of the IR pulse length allows for tuning of the temporal and spectral properties of the output radiation.

The FHI FEL facility, at the time of the workshop, included six experimental stations:

- Chemistry of transition metal clusters.
- Vibrational spectroscopy of gas-phase metal-oxide clusters.
- Vibrational spectroscopy of gas-phase clusters: ion solvation.
- Bio-molecules embedded in superfluid helium nano-droplets.
- Bio-molecules: IR spectroscopy combined with ion mobility spectrometry.
- Nonlinear spectroscopy of solids.
In addition one station devoted to vibrational spectroscopy of surface-deposited clusters was under preparation. Here one will measure the vibrational spectra of the clusters by recording the desorption signal of rare-gas atoms attached to the clusters.

In his presentation Wieland specifically focused on the experiments of bio-molecules embedded in helium nano-droplets. The He nano-droplets are formed by expanding cold He gas at high pressure into vacuum. They are produced at sizes of $10^4$-$10^6$ He atoms and by traversing an ion-trap they pick up the biomolecule. The He nano-droplets have many advantageous properties for spectroscopic experiments. They are ultra-cold ($T=0.38$ K), superfluid, have weak interactions with the incorporated molecules, and are optically transparent from deep UV to far IR. The low temperatures provide spectra with much narrower lines compared with gas-phase spectra using conventional techniques. High resolution spectra have already been measured of the protein angiotensine and the peptide leucine enkephalin, at the FHI FEL.

“Design and science of a Swedish THz free-electron laser” – Peter Salén (Stockholm University)

The development of new sources generating high-quality radiation in the THz-gap (0.1 – 10 THz) has led to an increased activity of research within this spectral region. As a response to the growing interest in THz radiation the Stockholm-Uppsala FEL centre has started the design of a THz FEL based on superconducting technology. In this talk the design of the envisioned light source was described and examples of scientific applications were presented.

THz sources can be divided up into the laser-based and accelerator-based categories. In the former type an optical pump pulse is typically converted into a THz pulse in a nonlinear crystal or a gas. This provides a compact setup which generates broad band pulses with relatively low repetition rate and average power. In contrast, the accelerator-based source, which produces THz radiation from high energy electron bunches that are guided through e.g. an undulator, offer a high repetition rate and average power, synchronization with an X-ray source, easy tunability, and potentially narrow-band pulses. The THz FELs are accelerator based sources and can be separated into super-radiant and cavity-based FELs. In the former the electrons emit THz rays coherently via the super-radiant process when passing through the undulator, and thus requires short electron bunches (~100 fs for 1 THz radiation). In the cavity based THz FEL two cavity mirrors guides the THz pulses repetitively through an undulator located between the mirrors. By overlapping each new electron bunch with a THz pulse in the cavity the intensity of the latter builds up every round trip. In the super-radiant THz FEL the THz pulses only pass once through the undulator which makes it more flexible with respect to the repetition rate compared with the cavity-based option, but the requirement of bunch compression down to ~100 fs is very challenging. The cavity based THz FEL puts
less demands on the electron bunches and this design has been proven in e.g. Neijmegen (FELIX – IR, FLARE – THz), Berlin (IR FEL), and Dresden (FELBE – MIR, FIR).

A preliminary design of the THz FEL proposed by the Stockholm-Uppsala FEL centre, and its THz output, is displayed in Fig. 3. In this highly flexible combined X-ray and THz source the electron bunches are accelerated by superconducting cavities to an energy of ~15 MeV and compressed to a bunch length of 1-10 ps. These bunches are then used for generation of X-ray pulses by e.g. inverse Compton scattering where photons from a high intensity IR beam scatters on the electron bunches. A bending arc finally guides the electrons to the THz FEL cavity located on top of the RF linac. Simulations have shown that pulse durations down to 6 periods is possible with this cavity, which corresponds to 1 ps at 6 THz (sub ps pulses may be achievable with short electron bunches at the bending magnet). The bandwidth is a few percent, but by phase locking the THz pulses in the cavity using an interferometer, bandwidths down to $10^{-4}$ may be achieved. The THz pulse repetition rate is 176 MHz out from the FEL cavity but the plan is to use mirrors after the cavity which only reflect after exposure to IR pulses, and thus by directing a 1 kHz IR laser beam onto the mirror, one may couple out at this repetition rate.

![THz FEL diagram](image)

**Fig. 3.** Design and output of the envisioned Stockholm-Uppsala THz FEL.

The electron bunch time-structure is shown in Fig. 4. The advantage of superconducting cavities is that they can supply the electron bunches with higher average power, and thus the proposed long macro bunches of 10 ms are possible. This enables about 100 times more THz
output average power for the proposed superconducting THz FEL compared with a normal conducting machine such as those at Nijmegen and Berlin, which is useful e.g. for spectroscopy in gas phase.

Fig. 4. Electron bunch time-structure at the end of the linac.

Peter gave a few examples of scientific applications for the envisioned light source. THz waves probe global motions of the molecule and are sensitive to its structure. Structural determination of molecules in gas phase samples can be extracted from THz vibrational spectra obtained by action spectroscopy, [5], as described in more detail in the next talk by Vasyl Yatsyna. These measurements request a high photon flux and are thus very suitable for a high average power THz FEL.

In THz solid state studies one often analyzes the conductivity extracted from reflection or transmission measurements. Here THz time-domain spectroscopy has been an important tool with its ability to measure both the amplitude and phase of the field, which provides direct extraction of both the imaginary and real part of the conductivity. Specifically, this has been successfully utilized in studies of superconductors, such as that by D. Fausti et al. [6] where light induced superconductivity was observed with a THz probe.

THz pump - X-ray probe experiments can be a beneficial tool for investigations of spin dynamics. In multiferroic materials different ferroic orders coexist and one may control the magnetic order with the E-field of the THz pulse. This was demonstrated by T. Kubacka et al. in [7] and could be important for the development of ultrafast magnetic control. Other possibilities with the THz pump - X-ray probe option are studies of THz-induced protein folding or phase transitions probed by X-ray diffraction.
Vasyl Yatsyna talked about the possibilities with a THz FEL for gas-phase spectroscopic studies by probing low-frequency vibrations. These experiments can be important for the understanding of larger biological systems e.g. by investigation of its smaller components, such as an amino acid sequence that is part of a larger protein. Low frequency vibrations may intuitively be understood to probe the larger structures of the molecule by analogy with the vibrations of a block attached to a spring where a larger mass leads to lower frequency vibrations. Hence, while IR radiation probes local modes, the THz range probes the non-local modes and, by the same block and spring analogy, the weak forces between atoms. In his talk he showed that the investigation of the IR/THz frequency vibrations of the molecule is useful for molecular structure determination. Resolving molecular structure is motivated by the fact that it defines function. He exemplified this by the oxygen transporting hemoglobin, which has four oxygen binding sites, and for which a huge conformational change takes place after binding the first oxygen, thereby reducing the binding affinity for the other binding sites.

Vasyl listed three main motivations for gas-phase studies using IR/THz spectroscopy,

- distinguish between intrinsic molecular properties and influence of environment
- study conformational landscapes
- support *ab initio* calculations

Fig. 5. IR-UV double resonance ion dip setup at FELIX.
Typically action spectroscopy is employed in gas-phase studies, where the IR/THz absorption is measured indirectly by monitoring its effect on some other process e.g. ionization. In the IR-UV double resonance ion dip technique, a UV laser is tuned to an intermediate level of the molecule and gets ionized by 2-photon absorption. When the IR laser is at resonance with a vibrational level, the ground state depletes and prohibits double ionization, which causes a dip in the ion signal. By scanning the IR frequency an IR absorption spectrum is acquired. Using this technique the structure of the molecule can be extracted by comparison with calculations. This has been done at FELIX using the setup shown in Fig. 5 and Vasyl presented an example of peptide conformational determination [5]. In this work the comparison of the experimental and calculated spectra in the 1000-1800 cm\(^{-1}\) range permitted the determination of the conformation of the Ac-Phe-Ala-NH\(_2\). However, for Ac-Phe-Gly-NH\(_2\) it was not possible to uniquely determine the conformation in this frequency range. But by moving to the far-IR region, measuring at 100-800 cm\(^{-1}\), they could distinguish between the conformers. As discussed after the presentation, this shows the usefulness of the far-IR region for structure determination using action spectroscopy, but the sub 100 cm\(^{-1}\) frequency range is still unknown territory.

Vasyl concluded that a THz FEL with high spectral power and resolution is a perfect tool matching needs for sophisticated experiments in molecular spectroscopy. Development of novel theoretical approaches to describe vibrational response of larger (biological) molecules is needed.

“Terahertz electronics” – Serguei Cherednichenko (Chalmers University of Technology)

Serguei Cherednichenko works at the Terahertz and Millimetre wave Laboratory which belongs to the Institute of Microtechnology and Nanoscience (MC2) at Chalmers. At MC2 they focus on applied and fundamental physics, and electronics research. The THz and mm lab together with the Microwave electronics lab house equipment for THz devices characterization and experiments on novel THz techniques. Recently MC2 received a 39 MSEK infrastructure grant from KAW to build up a laboratory for development of technology in the THz gap which will be recognized as an official research infrastructure.

Serguei described the THz projects at MC2 which include development of THz sources, detectors, and electronics. In order to increase the frequency of the output from signal generators, electronic frequency multipliers are used. They are working on the development of such devices based on e.g. Schottky or HBV (Heterostructure Barrier Varactor) diodes, and the characterization of their output. HBV type multipliers provide high output power of >100 mW at 1 GHz and on the order of 1 mW close to 1 THz. They are also very compact which is an important requirement for device-circuits. One goal is to develop high power THz multipliers based on multiplier arrays (Fig. 6) that step wise increase the frequency by a factor 3. The aim is to generate powers of 1 W at 300 GHz and 20 mW at 1 THz. He also described
their work with bolometer type THz detectors using YBa2Cu3O7-x (YBCO) thin films and the characterization of their response at the 0.3-1.6 THz region. The bolometer measures the radiation via heating of a material with a temperature-dependent electrical resistance. The YBCO based bolometers have shown potential to develop with respect to, e.g., responsivity and response time. They have also worked with THz-detectors based on graphene [8].

The THz electronics developed at MC2 have found various applications. Bolometers have been used for 1.4-1.9 THz low noise detection onboard the Herschel Space Observer as part of molecular line observations. They have also designed a THz gas spectrometer in the 300-500 GHz frequency range. It is suitable for spectroscopy of high temperature gases (up to 800 °C) and can be used in industrial applications, e.g., for precise water concentration and temperature monitoring in high temperature combustible gases [9]. Furthermore, they work with THz electronic applications in the field of high speed millimeter wave links.

Serguei concluded that they would be interested in using a THz FEL for verification of their THz multiplier sources, and for material analysis.

“Charge carrier dynamics of oregano metal halide perovskite solar cell probed by time resolved THz spectroscopy” – Carlito S. Ponseca, Jr. (Lund university)

Carlito Ponseca first presented previous work on organic, quantum dot sensitized and inorganic nanowires (see the summary of his talk from the 2013 workshop). Then he turned to their studies of the organometal halide perovskite (OMHP) solar cell material CH3NH3PbI3 [10]. OMHP-based solar cells have been shown to provide high conversion efficiencies of up to 15%. However, many of the fundamental photophysical processes remain poorly understood. They investigated the transport properties of pure CH3NH3PbI3, and also of CH3NH3PbI3 introduced in the open voids of Al2O3 nanoparticle structures in order to understand the influence of the nanostructure on the charge carrier dynamics. Furthermore, CH3NH3PbI3 on TiO2 was measured in order to clarify the role of an electron accepting metal
oxide on the excited state dynamics in the perovskite. Using a combination of the time resolved spectroscopic techniques; transient absorption, time-resolved terahertz spectroscopy, and time-resolved microwave conductivity, they could monitor the carrier dynamics on the timescales of less than 1 ps to over 100 µs. Their measurements show nearly ideal solar cell properties for neat CH₃NH₃PbI₃ and CH₃NH₃PbI₃/Al₂O₃, with ultrafast formation of highly mobile charges in about 2 ps, and a balanced mobility between electrons and holes that persists on a microsecond timescale. In contrast the CH₃NH₃PbI₃/TiO₂ displays a lower overall mobility due to the electron injection to the TiO₂, which has a very low electron mobility (Fig. 7).

Fig. 7. Illustration of the mobility of electrons and holes for CH₃NH₃PbI₃ on TiO₂ and Al₂O₃, respectively.

Carlito pointed out that THz waves can be utilized in ultrafast THz scanning tunneling microscopy for simultaneous temporal and spatial characterization of charge carrier dynamics. In this technique a THz pulse is focused on the scanning probe tip of a scanning tunneling microscope (STM), and thus creates a voltage transient that drives the electrons across the probe-sample junction, which creates a current that is sensitive to the spatial structure. In this way the THz-STM combines the high spatial resolution of an STM with the subpicosecond time resolution of THz pulse spectroscopy. Previous efforts of integrating femtosecond laser pulses with STMs have been limited at ~10 ps temporal resolution with nanometer spatial resolution. Now using the THz-STM, <0.5 ps and 2 nm resolutions have been accomplished [11]. It has been applied to time resolved measurements of the excitation and decay dynamics of an InAs nanodot using an 800 nm pump pulse and a continuously delayed THz pulse focused to the probe tip. The THz-STM could be an essential tool for resolving ultrafast dynamics within nanoscale device structures.

“Strong single-cycle THz fields” – Stefano Bonetti (Stockholm University)
Stefano Bonetti gave an overview of single-cycle THz sources and their applications based on his experience with such work. Laser generated THz sources function by inducing a nonlinear polarization in a crystal or gas using a strong laser pulse. It takes advantage of the widespread availability of table top optical lasers based on regenerative amplification which provides ~1 kHz repetition rate, 5 mJ/pulse, and 50-100 fs long pulses. THz generation via optical rectification is a commonly used method in which the nonlinear polarization is generated in a crystal with a second order nonlinear susceptibility, $\chi^{(2)}$, by the strong incident laser field from the ultrashort laser pulses. The second order nonlinear polarization acts as a source for radiation by Maxwell’s equations, which forms a single cycle pulse of THz frequency. In order to achieve efficient THz generation the THz waves must be phase matched such that they add up coherently through the crystal and this is accomplished when the group refractive index of the incident laser pulse equals the phase refractive index of the THz radiation. A commonly used crystal material for optical rectification is ZnTe because it is naturally phase matched for THz and 800 nm pulses. Another popular material is LiNbO$_3$ which can produce high conversion efficiencies, but has a bad phase matching which results in THz pulses that are outcoupled at an angle to the incident laser beam. Using incident laser pulses with a pulse front tilt one may get around this phase matching problem. Although the THz generation is extremely efficient in the LiNbO$_3$ crystal, outcoupling and absorption still limit the useful radiation.

Stefano further described single-cycle THz sources based on plasma generation. Here intense femtosecond laser pulses focused in a gas (e.g. air, N$_2$ or noble gases) creates a plasma which emits broad band THz radiation. The most common technique employs both 800 nm and 400 nm incident beams that are mixed in the plasma. Although the process is not fully understood it is believed that the THz radiation is produced because tunnel ionization of the atoms create a plasma of free electrons and positively charged ions, where the free electrons emit THz waves as they are further accelerated by the applied field [12].

A comparison between the output pulse characteristics of the LiNbO$_3$ [13] and plasma [14] sources was presented. Both sources produce single cycle pulses but the plasma source (with N$_2$ gas) yields a considerably broader spectrum (Fig. 8) but with lower peak field.
Stefano and his collaborators (M. Hoffmann and H. Durr in particular) have performed experiments at SLAC using single-cycle THz pulses generated via optical rectification of a \(\sim 100\) fs, 800 nm, 4 mJ laser pulse in a LiNbO\(_3\) crystal.

In a laser lab, \textit{i.e.} using a fraction of the 800 nm light as a probe, they demonstrated control of the magnetization in a thin film ferromagnet (CoFeB) both at fast time scales (direct torque of the THz H-field on the magnetization) as well as on slower ones, confirmed by the observation of ferromagnetic resonance oscillations.

At LCLS, Stefano was also part of the experimental teams that used femtosecond X-rays to measure ultrafast X-ray diffraction in samples pumped with single-cycle THz fields. He presented two experiments. The first was the observation of an insulator-to-metal phase transition in VO\(_2\) induced by the strong THz radiation. The remarkable result of this experiment is that the lattice phase transition occurs \(\sim 10\) ps \textit{after} the electronic one. Typically, when one induces a phase transition either via temperature or optical laser pulses, the two sub-systems (the electrons and the lattice) are strongly coupled, and the lattice moves together with the electrons. The fact that THz radiation can be used to potentially drive a purely electronic phase transition, opens up for the use of correlated materials in the electronics beyond silicon.

The second LCLS experiment was the attempt to drive a coherent excitation of a soft-phonon mode in the model perovskite system SrTiO\(_3\). Such compound is not ferroelectric, but it becomes ferroelectric upon slight doping and below a certain critical temperature \(T_c\). The exact mechanism for the normal-to-ferroelectric transition in these compounds is not yet completely understood, but there is evidence that a soft phonon mode of diverging amplitude as \(T_c\) is approached may be the key-player in the transition. SrTiO\(_3\) shows no finite \(T_c\) (i.e. it never becomes ferroelectric), but there are nonetheless indications of a soft phonon mode of diverging amplitude as temperature is lowered. The experimental team attempted to drive this

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig8.png}
\caption{THz spectra generated by a) optical rectification in a LiNbO\(_3\) crystal [13], and b) a nitrogen plasma source [14].}
\end{figure}
soft phonon (at ~1 THz) by direct coupling of the THz electric field with the polarization of
the perovskite unit cell, i.e. by "dragging" atoms directly, and to observe such atomic
displacement in a time-resolved X-ray diffraction signal. This was a shorter, "in-house" LCLS
beamtime, but they nevertheless found evidence that the atoms respond to the THz excitation
with a characteristic frequency of about 1 THz, consistent with the soft-phonon mode picture.

Single cycle THz pulses may also be produced via coherent transition radiation (CTR) by
directing short electron bunches onto a metal foil. When the electrons travel between
media with different dielectric constants, transition radiation is emitted. Electron bunches
that are short with respect to the generated waves will emit coherently via a super-radiant
process. Using high-energy linear accelerators THz pulses with extremely strong peak fields
can be generated. Stefano has experience as a user of the THz light source at the FACET
(Facility for ACcelerator science and Experimental Tests) facility at SLAC [15]. FACET
provides a 23 GeV electron beam which allows compression of the electron bunches to sub
picosecond duration and thereby coherent generation of intense single-cycle THz pulses via
CTR. Peak fields of 0.6 GV/m have been achieved. The CTR produces radially polarized
pulses and therefore a polarizer is used for creating linearly polarized light.

Stefano concluded by defining the characteristics of the “dream” THz source:

- Can produce both broad- and narrowband THz fields => Combination of THz FEL
  with laser based source.
- Can be used to do pump-probe experiments => Match with typical laser sources (1-10
  kHz)?
- Can probe the nanoscale (a “Tera-nano” facility) => Scanning probe microscope
  (STM, AFM, MFM…) built in?
- Can be the new tool for nonlinear THz science => High pulse energy available?

“Spin dynamics in THz regime” – Corina Etz (Uppsala University, Luleå Technical
University)

Corina Etz presented a theoretical view on spin and magnetization dynamics. The
magnetization dynamics can be investigated at dimensions ranging from Ångström
(subatomic spins), via nanometer (atomistic spin dynamics), to micrometer and millimeter
(magnetization as m(r)), and on time scales from attoseconds to seconds. The THz time scale
corresponds to about a picosecond and is suitable for such studies. At Uppsala they have
developed a simulation tool for atomistic spin dynamics called UppASD [16]. It provides
static and dynamic information of materials that can be directly probed in experiments using
techniques such as inelastic scattering, ferromagnetic resonance (FMR), superconducting
quantum interference device (SQUID), and Magneto-optical Kerr effect (MOKE).
As an example of what can be done with the UppASD simulation program, Corina presented recent investigations of the magnetic properties of low-dimensional ferromagnets [17]. They simulated the magnon (quantized spin wave) spectra for different thicknesses of a magnetic material on a substrate at finite temperatures. The systems chosen had been extensively studied previously using spin-polarized electron energy loss spectroscopy (SPEELS) which recently has become a powerful technique for investigating spin waves at surfaces and in thin films [19]. Figure 9 displays an example of a spin wave dispersion spectrum for two layers of Fe on W(110) at 300 K that shows good agreement with SPEEL experiments [20]. She also explained that UppASD has potential for other applications such as for simulating logical devices based on spintronics.

Fig. 9. Spin wave dispersion spectrum obtained from ASD simulations for two layers of Fe on W(110) at 300 K [17]. White squares are experimental values.

In conclusion, within ASD they can investigate static and dynamic properties accessible in experiments, and predict novel properties and design future devices.
“THz ellipsometry and optical Hall effect” – Vanya Darakchieva (Linköping University)

Vanya Darakchieva is the head of a group that develops ellipsometric methodologies and applies this technique to characterization of materials for high-speed electronics with respect to charge transport and structural properties. Ellipsometry measures the change of the polarization state of linearly polarized radiation upon interaction with a sample and allows calculation of both the real and imaginary part of the dielectric function by applying a model for layer structure of the actual sample. It can be used for determination of material properties such as optical constants, conductivity, and thickness. It functions at a large wavelength range from VUV-VIS-IR-THz. THz ellipsometry is so far commercially unavailable but can be applied to many different research areas such as semiconductors, superconductivity, magnetism, low-dimensional effects, strongly correlated electrons, and biomaterials.

By applying a magnetic field to the sample more information can be extracted via the optical Hall effect. The magnetic-field induced birefringence by free charge carrier excitations from interaction with the radiation can be measured with ellipsometry. This so called magneto-ellipsometry provides information about charge carrier properties such as concentration, mobility, effective mass, and carrier type. One such instrument has been constructed in Nebraska (Fig. 10) which covers an ultra wide spectral range of 0.1-210 THz (0.4-870 meV). Vanya’s group have been using this facility and plan to build an improved version of this unique ellipsometry setup that will be the core of a new facility for THz materials preparation and analysis. The THz source employed in the setup is a backward wave oscillator which produces powers of 1 μW- 0.1 W in the frequency range of 0.1-1.6 THz and emits linearly polarized light. This will be the first THz ellipsometer in Europe and provides a noncontact, non-destructive method for measuring electronic transport properties, thereby avoiding surface damage and sample contamination. Using the optical Hall effect it is also possible to differentiate between conductive channels in multilayered structures, access confined carriers in nanostructures, and acquire charge carrier properties, such as concentration, mobility, effective mass, and carrier type. The research objectives are to use the THz magneto-ellipsometer for characterization and feedback at materials fabrication, e.g. growth of wafer-scale graphene and group-III nitrides which will lead to progress in novel technologies and functionalities based on these materials, such as THz electronics.
Vanya presented a number of experiments that have been performed using THz ellipsometry and optical Hall effect. Group-III nitride heterostructures have a strong potential for high-power/high-temperature devices for GHz and THz frequency applications. AlGaN/GaN heterostructures are of particular interest due to the formation of a two-dimensional electron gas (2DEG) with high sheet charge density. The development of these types of high electron mobility transistors requires a thorough insight into the charge carrier properties such as mobility, sheet charge density, and effective mass. The temperature dependence of these parameters for the 2DEG in AlGaN/GaN heterostructures (Fig. 11) were measured using the THz optical Hall effect in the 0.22-0.32 THz spectral range and for temperatures between 1.5 K and 300 K [20]. The temperature dependence of the sheet density and mobility can be determined by electrical methods, but the effective mass measurement is typically carried out at low temperatures because the applied techniques require high mobilities. They found good agreement with previous electrical measurements for the sheet density and mobility. An increase of the effective mass with temperature was observed and was interpreted as an indication for a reduction in 2DEG spatial confinement at room temperature.
At Linköping University they produce epitaxial (single or few layers on a substrate) graphene by high-temperature sublimation on SiC. These graphene sheets are very promising for large-scale manufacturing of novel fast electronic devices [21]. THz and IR ellipsometry and optical Hall effect measurements were conducted in order to investigate the properties of the epitaxial graphene sheets [22]. They determined the hole mobility, density, and effective mass in epitaxial graphene which displayed differences between those grown on Si- and C-face 6H-SiC substrates. The C-phase grown graphene furthermore displayed two layers with different carrier density and mobility, while a single-channel conduction process was identified when grown on the Si-phase.

Finally, Vanya described THz ellipsometry measurements performed on a metal slanted columnar thin film [23]. Such sculptured thin films are materials with a spatially coherent columnar nanostructure that can be grown in a controlled manner and designed with specific optical properties in the THz range. The THz ellipsometry revealed the material’s anisotropic THz optical properties.

Vanya suggested that a THz FEL could be useful for THz time resolved ellipsometry where the full waveform of the reflected or transmitted THz pulse is recorded [24], and also for studies of nonlinear phenomena. She further suggested that a THz ellipsometer could be a possible instrument for a FEL. For ellipsometric measurements a linear polarization would be required.
“Terahertz for biomedical applications: activities in the Microwave & techn. group at Uppsala University” – Dragos Dancila (Uppsala University)

Dragos Dancila presented the THz related activities of the microwave group at Uppsala University, which has a broad experience with microwaves and mm-waves for imaging and bio-medical applications. They are involved in several EU and national projects, such as development of radiometers for passive mm-wave imaging (NANOTEC), Rx/Tx THz generation based on NLTL (nonlinear transmission line) CMOS (complementary metal-oxide-semiconductor) components (EU project ULTRA), and skin cancer detection using mm-wave silicon wave guides (Vinnova).

Using THz plasmonic antennas they have investigated the enhanced detection sensitivity of cells. The plasmonic antennas exploit the field enhancement from collective electron oscillations in a metal. Here they employ a structure of two silicon based triangles with a small gap between the narrow parts, where the field is enhanced. Using THz time domain spectroscopy (TDS) applied to a thin bacterial film deposited on top of a chip with plasmonic antennas they demonstrated enhanced selective detection of bacteria types [25]. From the frequency shift of the recorded THz spectra, and difference in transmission at specific THz frequencies they were able to distinguish between different types of bacteria. It was also possible to separate between live and dead bacteria.

In another project they have developed and tested a mm-wave probe for skin cancer diagnosis, which is based on the discrimination of tissues of different water content [26]. They aimed at improving the spatial resolution by using a miniaturized probe.

Dragos draw attention to the capabilities of THz spectroscopy for studies of protein dynamics. In an experiment using THz-TDS it has been demonstrated that the THz radiation is a convenient probe of conformational changes in proteins in solution [27]. They observed a clear increase of absorption at THz frequencies for the 450 nm induced partial unfolding of photoactive yellow protein (Fig. 12). Dragos suggested that such protein dynamics could be a possible scientific application for a THz FEL.

![Fig. 12. Partial unfolding of photoactive yellow protein [27].](image-url)
He concluded by informing that the microwave group at Uppsala could contribute with THz detectors, plasmonic antenna, bio-electromagnetics expertise, as well as preliminary experimentation with available THz-TDS up to 4 THz.

“Spectroscopy of negative ions” – Dag Hanstorp (University of Gothenburg)

Dag Hanstorp talked about spectroscopy of negative ions, and in particular about their use for studies of orbital alignment in atoms. Negative ions have a number of characteristic properties, such as a small binding energy (~1 eV), few excited states, almost no excited states with opposite parity and therefore no optically allowed transitions, and electron correlations are significant since they are required to bind the electrons to form a stable system. Applications involving gas phase negative ions can be found in accelerator mass spectrometry, controlled fusion, astrophysics, atmospheric physics, and plasma studies.

Dag described experiments performed to investigate the orbital alignment of atoms generated by electron photodetachment of negative atomic ions in a strong laser field, and its dynamics [28]. The induced orbital alignment is explained by the much higher electron tunneling rate at strong laser intensities for magnetic quantum numbers m_l=0 than for m_l≠0. This leads to primary ionization of the m_l=0 orbitals and thus a hole in the electron density distribution of the formed neutral atom that is oriented along the laser polarization. A pump at λ=2055 nm was used for photodetachment and a variably delayed probe at λ=1310 nm monitored the electron density distribution (Fig. 13). The strong probe field ionized the spatial portion of the electron density distribution oriented along the laser polarization axis and thus allowed the distribution to be visualized by electron imaging. The oscillating alignment dynamics of ~1 ps period observed in the C atom originates from quantum beats between three coherently excited states of J=0, 1, 2. The demonstrated possibility to initiate and monitor electron motion in neutral atoms can be useful for control of chemical reactions by preparing the atoms with a specific electron density distribution.
“A quest for Fröhlich’s condensation in proteins” – Gergely Katona (University of Gothenburg)

Gergely Katona’s research group studies biological molecules using X-rays and THz radiation. One exotic idea of relevance for the THz frequency range, was suggested already in 1968 by H. Fröhlich [29]. He proposed that biological processes, such as cell division, are influenced by collective coherent long-range vibrational motions in the THz range. These ideas have also lead to questions about the effect of non-ionizing radiation on macromolecules, e.g. does it alter enzymatic activity, and are there irreversible changes from altered activity that can lead to cancer? In this respect one has to deal with issues related to mobile phones, WLAN, etc.

Gergely presented an experimental study where they aimed at visualizing THz resonances in proteins by X-ray crystallography using lysozyme (Fig. 14) as a modelsystem. Their experimental strategy was to align the crystal plane normal with the rotation axis and collect a 360° dataset with fine slicing per crystal. Several datasets were merged in order to enhance the signal. Difference electron density maps were then calculated from these data sets where the electron density from the THz-exposed crystals were subtracted by that from the unexposed crystals. In order to distinguish from thermal effects the measurement were performed with alternating on and off THz-exposure. They found a THz induced electron density difference at helix 3 in lysozyme for 0.4 THz illuminated crystals, but no such effect for 0.2 THz exposure. These electron differences are associated with vibrational motions that have a long duration. The origin of these long lived states are considered unlikely to be thermal or radiation damage effects, but instead they concluded that they probably are related to a Fröhlich process where vibrational modes condensate into one long lived collective mode.
Gergely went on to describe the possible role of electromagnetism, and specifically THz radiation in living organisms. Examples of what may be explained by THz radiation induced changes are dominant principles such as statistical thermodynamics in enzyme catalysis and protein-protein or protein-ligand recognition, and reaction diffusion systems in biological pattern formation (e.g. stripes on zebras). Figure 15 shows a schematic illustration of the organizing principles of life.

He finished by describing in his opinion low-risk and high-risk life-science experiments with a THz FEL and X-ray source. Low-risk experiments suggested were of THz pump-X-ray probe type using crystallography or solution scattering probing. Here a low X-ray flux is acceptable and a high repetition rate likely achievable. Interesting questions are, which part of the protein responds, and how fast are motions dampened? High-risk experiments could be designed to answer questions such as, what is the influence of THz radiation on biochemical
reactions, and biological pattern formation? Since biology is slow it is necessary to be able to design long experiments, and continuous rather than low repetition rate excitation is advantageous. He noted that a wide range of frequencies and power levels, as well as adjustable exposure area is desired in this highly exploratory field.

“Short pulses or high energy resolution? At a crossroad for a THz FEL for spectroscopy” – Olof Karis (Uppsala University)

Olof Karis is the head of the molecular and condensed matter physics department at Uppsala University. There they perform research on light-matter interactions at the atomic level for understanding and control of electronic properties for energy and environmental applications, and for new functional materials. This includes studies of magnetic materials for which the magnetization dynamics can advantageously be investigated using frequencies in the GHz-THz range. These dynamics can proceed on femtosecond timescales and need suitable probing techniques. Olof exemplified by an experiment where time-resolved X-ray magnetic circular dichroism was employed as a layer-specific, phase-resolved probe of GHz driven magnetization in a heterostructure [30]. Here they observed large phase variations of the magnetic field between layers in contrast to previous assumptions that they are zero. This may have implications for the identification of novel effects in spintronics. In another experiment spin currents were detected on ultrafast time-scales in magnetic multilayer structures using a high harmonic generation (HHG) source to record the transverse magneto-optical Kerr effect (T-MOKE) in the XUV spectral range [31]. T-MOKE measures the relative difference of the sample reflectivity at distinct magnetization directions and is an efficient tool for magnetization monitoring. The magnetization dynamics were excited with an optical femtosecond laser and probed at the absorption edges of the layer elements which provided layer specific detection.

At Uppsala the HHG source HELIOS (High Energy Laser Induced Overtone Source) has been developed since 2010. It generates XUV photons between 10-100 eV and monochromatized pulses with <20 fs duration and is pumped by an optical laser providing femtosecond pulses at λ=800 nm and at a repetition rate of 5 kHz. HELIOS also includes an optical parametric amplifier producing wavelengths of 240 nm–20 µm for pumping of the sample. Some first results have been obtained from experiments using e.g. ARPES on graphene, and T-MOKE on a permalloy. Olof indicated the possibility of combining the THz FEL with a HHG source, motivated by the potentially higher photon energy reachable with a longer pumping wavelength than the traditionally used near-IR frequencies [32]. However, it was pointed out in the discussions of the talk that wavelengths above ~10 µm are difficult for generation of HHG because of issues such as unrealistic gas pressures needed for phasematching in the gas.
Although HELIOS is used for magnetic studies, a more selective pump would be in the THz regime because many quasi-particles (phonons, magnons, polaron, polaritons) in solid-state physics have characteristic energies in the meV range. As examples of what could be studied using the THz pulse as a pump, Olof mentioned spin dynamics of high magnetic anisotropy materials [33], and experiments on multiferroic materials [34] in which control of the magnetism can be obtained via the electric field e.g. from a THz pulse. He also described an experiment where the THz pulse functions as a probe of screening clouds (Fig. 16) formed around charges in plasmas [35]. In this experiment they directly observe the formation of these dressed quasi-particles in a photo-excited electron-hole plasma in the semiconductor GaAs. They employ electro-optic sampling of the probing single-cycle THz pulse which is temporally delayed with respect to the optical femtosecond pump pulse. This allows them to monitor the changes in the probe electric field as a function of time, from which they can extract the time resolved dielectric function in the 0-35 THz range, and thus information about the formation time of the dressed quasi-particles.

Fig. 16. Sketch of the transition from randomly distributed charges to screening clouds induced by an optical pulse, which can be probed with THz pulses [35].

“Synthesis and characterization of carbon-based nano-materials: what can be done using THz spectroscopy” – Alexander Soldatov (Luleå University of Technology (LTU))

Alexander Soldatov is the leader of the high-pressure spectroscopy group at LTU where they study carbon-based nanostructures (C_{60} (fullerene), carbon nanotubes (CNT), graphene) at high pressures. Specifically graphene and CNTs have a number of extraordinary properties,
such as their strength and flexibility, which allows them to be bent and buckled without breaking, as well as high current capacity and thermal conductivity. These characteristics make them suitable for applications in molecular electronics, energy storage, and superstrong materials. Reasons for using high pressure as a tool for research on these materials are that phase transitions occur at “low” (GPa) pressures, and that extreme pressure is required to probe how well the structure of the molecular units are maintained (structural integrity). Compression of carbon materials is of interest due to the possibility of producing diamond from graphite, polymerization of known carbon allotropes (new superhard materials and other properties), and creating new phases of carbon. In their group they have equipment for generating ultra-high static pressure up to 2-4 Mbar (200-400 GPa) and temperatures up to 600 °C in a diamond anvil cell, as well as dynamic pressures up to 1 Mbar. The characterization methods used are for example Raman and FTIR spectroscopy, and different forms of microscopy.

Alexander described their studies on different carbon nanostructures. Fullerene molecules polymerize into 2D structures at high pressure (Fig. 17) and temperature and the possibility has been suggested to form 3D polymers by applying uniaxial pressure on 2D polymers [36]. Alexander and his group have performed experiments on phase transitions of fullerene polymers by means of Raman spectroscopy and resistivity measurements as a function of pressures up to 33 GPa. [37,38] They did not observe signatures of 3D fullerene polymers but showed that the 2D polymeric phase survived 33 GPa of non-hydrostatic pressure, which makes them more stable at high pressure than monomeric C_{60}. Moreover, they observed a significant decrease of the resistance at 20-25 GPa, but the metallic character of the high-pressure phase is still to be proven. Alexander suggested that this possible insulator-metal transition could be further investigated using broad-band THz spectroscopy, which would have the advantages of no electrical probes attachment, possibility to monitor band gap closure via photoconductivity, and that no high energy pulses are required.
CNTs are graphene sheets rolled up into a cylindrical tube and can be produced as single wall CNT (SWCNT) or multi wall CNT, defined by the number of tubes of different diameters. The Raman spectrum is able to characterize the nanotubes via vibrational modes, such as the radial breathing mode, which reveals the tube diameter via its frequency, or modes related to defects. From the intensity of these modes the structural state of the CNT can be monitored. They have compared the structural integrity of SWCNTs at high static and dynamic pressure in order to probe the strength of the material by means of Raman spectroscopy and transmission electron microscopy, and showed that the dynamic pressure of 36 GPa completely destroys the sample, while the SWCNTs partially survive the corresponding static pressure [39]. The shock pressure limit for structural integrity of SWCNTs is established at 26 GPa, which underscores the unmatching capability of CNTs to withstand extreme dynamic loads. Further studies are needed to ascertain the structure of the new high-pressure phases and Alexander suggested X-ray diffraction measurements of laser-shock induced dynamic pressures [40], and broad band THz spectroscopy (1 THz central frequency, 1.5 THz bandwidth) for static pressures.

Raman spectroscopy was utilized for pressure dependent experiments on graphene where they have performed the first study of free standing material monolayer under extreme pressure in a diamond anvil cell. The technique allowed them to obtain important reference data for graphene-based materials, which are crucial for further investigations of strain on graphene and tests of quality. One important property of double layer graphene is the possibility of

**One-dimentional polymer**
orthorhombic, $p = 8 \text{ GPa}, T = 300 \text{ C}$

**Two-dimentional polymers:**
tetragonal, $p = 3 \text{ GPa}, T = 600 \text{ C}$
rhombohedral, $p = 4 \text{ GPa}, T = 700 \text{ C}$

Fig. 17. Illustration of the 1D and 2D structures of fullerenes formed at high pressure.
introducing a band gap by introducing an asymmetry in the bilayer structure (single layer and double layer graphene normally lacks a band gap which limits their use in electronics). Alexander suggested that THz spectroscopy using broad band THz pulses would be useful for measurements of band gap opening in double-layer graphene under stress.

“Visualizing ultrafast structural changes in proteins using XFEL radiation” – Richard Neutze (University of Gothenburg)

Richard Neutze described experiments performed at LCLS using TR-WAXS (Time-Resolved Wide Angle X-ray Scattering) to measure ultrafast protein structural changes. Such protein conformational dynamics studies on a picosecond time scale are relevant as it has been indicated that initial photosynthetic charge separation is coupled to ultrafast protein structural changes. Further, they are required for a deeper understanding of how excess energy absorbed by light-driven proteins is dissipated before damage occurs. This process has been explained by a release of strain in the protein as a structural deformation that propagates away from the focus in the protein, a so-called protein quake. The experiments were performed on the photosynthetic reaction center of Blastochloris viridis (RC\textsubscript{vir}) (Fig. 18) which was multiphoton excited with an 800 nm pump laser and the ultrafast protein dynamics was visualized with TR-WAXS. By means of spectral decomposition they were able to separate the different processes of the protein dynamics and showed that structural deformations propagated away from the center of energy input faster than the heat transfer in the protein. These quake-like protein motions build up in picoseconds and decay in tens of picoseconds.
Richard noted that there are plans for generating THz radiation at the femtoMAX beamline at MAXIV. This will be produced via CTR by sending the electron bunches of the linac through a Be foil, and will thus be a broad band THz source. FemtoMAX can provide perfectly synchronized THz pulses that arrive before the X-ray pulses, which is important because the latter are more difficult to temporally delay. This source and the THz FEL planned by the FEL-centre could be used for THz pump-probe studies where the THz pulses selectively excite protein normal modes and drive protein dynamics, or in a generic approach to probe protein motions. Questions that could be investigated by THz pump-probe schemes are: do protein dynamical motions influence cell behavior, are ultrafast motions coupled to electron transfer, and can we excite and identify biological motions that persist for ns or µs.

“Stimulating surface chemical reactions with THz” – Anders Nilsson (Stockholm University/SLAC)

Anders Nilsson has extensive experience of research within surface science and of water, and here he presented his view on how THz radiation could be applied to these fields.

Catalysis is key to the production of sustainable fuel by conversion of biomass, electricity, and sunlight to fuel. Moreover it is highly important for the efficiency of the production of ammonia through the so-called Haber-Bosch process, in which the NH₃ is generated from a
reaction of N\textsubscript{2} with H\textsubscript{2}. This process has had a dramatic impact on the ability to grow food because of the use of fertilizers produced from ammonia. In this type of catalytic reaction, and in many other processes of importance for energy production and the industry in general, there has to be a reactivity balance \textit{i.e.} a balance between the atomic (N) bonding to the catalytic surface, and the molecular (N\textsubscript{2}) dissociation. This balance depends on the catalytic material and affects the reaction activity. A fundamental understanding of these elementary catalytic reactions is needed. One wants to find ways to overcome the fundamental limits of this reaction balance and coherent control could be one option.

Femtochemistry at metal surfaces driven by ultrashort optical pulses is dominated by substrate-mediated excitations \textit{i.e.} the hot electrons and excited phonons couple to the adsorbate and affects the reaction. However, this allows little control of the reaction pathway. THz radiation couples to many surface vibrations such as phonons and frustrated vibrations of the molecules bound to the surface. Using strong-field single cycle (or quasi half-cycle) THz pulses, with fields of \textasciitilde GV/m which corresponds to the Coulomb force between the electron and nuclei, one may therefore excite these vibrational motions impulsively and thus initiate a coherent motion. This allows coherent control of \textit{e.g.} the direction of motion of the molecule attached to the surface by changing the orientation of the polarization of the incident THz pulse (Fig. 19).

Fig. 19. Visualization of the control of the motion of a molecule attached to the surface, enabled by short strong-field THz pulses.

Another application of strong field single-cycle THz pulses is for triggering of an electrochemical reaction. The electrochemical double layer, which can exist on \textit{e.g.} an electrode where it affects electrolysis, consists of one negative and one positive layer on the surface in contact with liquid. The electric field holding this layer together is \textasciitilde1 GV/m and thus a THz pulse of this field strength may be used to break this field and thereby control the electrochemical reaction.

Anders presented preliminary experimental results performed at the LCLS where they produce THz pulses inside the undulator tunnel by directing the high energy LCLS electron beam onto a Be foil and thus generate short intense THz pulses (0.3 GV/m after focusing) via
CTR. The experiments demonstrated the use of short THz pulses for inducing CO oxidation on a Ru surface.

He further described how an FEL such as LCLS can be used for probing of THz induced processes. By using two synchronized electron bunches a THz pulse can be produced by the first bunch in e.g. a bending magnet and an X-ray pulse can be produced by a lower charge second bunch. This provides a suitable setup for THz induced surface processes probed by XAS (X-ray absorption spectroscopy), XES (X-ray emission spectroscopy) or XRS (X-ray Raman scattering).

To investigate the fundamentals of the above described THz induced surface processes one needs to have half cycle pulses with field strengths of 1-10 GV/m which can be provided by linac based sources such as those at SLAC, MAXIV, and DESY. One could also investigate lower energy and longer pulse ranges at the Stockholm-Uppsala THz facility, although it is unknown if this would work. For example, resonant excitation of adsorbate-substrate vibration, or selective mode excitation that could drive selectivity in catalysis.

Anders continued to talk about studies of water, which is still a far from well understood liquid. It displays a distinct behavior compared with a typical liquid for a number of thermodynamic observables, such as the isothermal compressibility, heat capacity, and thermal expansion. Characteristic for these three observables is that they are associated with fluctuations (density and entropy fluctuations) in the liquid which increase with cooling, contrary to a normal liquid. These properties are most pronounced in the supercooled regime in which water has a temperature below 0 °C but is still in liquid form. However, they can also be observed at ambient conditions and here X-ray studies have been helpful. For example XAS, XES, and XRS has been employed to understand the structure of water, and SAXS (small angle X-ray scattering) has been used for detecting density fluctuations [42]. They have suggested that the anomalous properties of water originate from increased density fluctuations when it is cooled down and that these density fluctuations are related to two distinct phases of water. One high density phase with strongly distorted hydrogen bonds that is dominant at higher ambient temperatures, and one low density phase with strongly tetrahedrally bonded molecules, which increases upon cooling as the patches of these structures expand (Fig. 20). The low frequency spectrum of water below 1000 cm⁻¹ is especially sensitive to the local molecular structure as it reflects the intermolecular dynamics and probes the H-bond modes. This frequency region has been used for such studies of water using time-resolved optical Kerr effect spectroscopy [43]. Here an optical pump pulse induced a birefringence in the sample and a time-delayed probe pulse measures the birefringence, which reflects the relaxation and vibrational response of the molecules. A Fourier transform of the response revealed the hydrogen bending mode at ~50 cm⁻¹ as well as two distinct modes at approximately 200 cm⁻¹ which appeared to be associated with the low- and high density phases of water.
Anders concluded that the Stockholm-Uppsala THz facility could be used for pump-probe measurements for slow time-scale motion in water, where probing may be accomplished with transient THz spectroscopy or diffusive X-ray scattering. Useful experimental conditions would be provided by a liquid jet and deep supercooling with water droplets.

“Time-resolved two-color spectroscopy in molecules” – Stacey Sörensen (Lund University)

Stacey Sörensen initially gave an overview of photochemistry and the methods used for studying photochemical reactions from a gas phase perspective, and then described what can be done with the proposed THz source. Examples of fundamental dynamics in molecules include ionization (photo-, auto-, single, double), isomerization (bending, bond rearrangement), dissociation, and vibration of molecules and clusters and many different techniques are employed to study these dynamics. They include ion imaging which gives information about the molecular geometry through the extracted momenta of the fragments. For example, the geometrical changes of small molecules upon core-hole excitation can be investigated [44]. Photoelectron spectroscopy has been used to study the influence of plasmon vibrations on the angular distribution of active electron orbitals [45] and various pump-probe experiments can be conducted in order to monitor molecular dynamics, such as the isomerization of XUV photoionized Acetylene [46]. She noted that low-pressure gases are characterized by strong, unique absorption signatures and that the THz spectral region is suitable for identifying compounds in a mixture of gases based on rotational transitions in the absorption spectrum.

Stacey considered the scientific potential of the proposed THz FEL to be:

- THz excited states: low-energy excitations or vibrational modes
- Aromatic molecules ring breathing modes
- Collective vibrational modes: fullerenes, molecular clusters, vibrational coupling to complexes
- Charge transfer in polymers

She exemplified with possible experiments for the THz source, e.g. excitation to higher bound levels of the ring puckering vibrational mode of Cyclopentane (~100 cm\(^{-1}\) bending out of the plane) [47] using THz radiation, where the ring geometry could be probed with X-rays.

Another relevant application for the THz source would be studies of water nanoclusters, which have been suggested to play a role in physics, chemistry, biology, and cosmology and possess unique vibrational modes in the 1-6 THz range [48]. The water nanoclusters exist in water vapor and that they are preferentially formed with specific molecular numbers and configurations that often have a spherical “bucky-ball” like structure and where common examples are \((\text{H}_2\text{O})_{20}\) and \((\text{H}_2\text{O})_{21}\text{H}^+\). These water clusters may interact with proteins via the THz vibrations and could be essential to biomolecular function, e.g. for protein folding where the misfolding of proteins, responsible for disfunction and disease, are likely associated with the failure to form clusters which properly interact with the protein. Moreover, the THz vibrations of the water clusters can interact with soot precursor molecules and lead to their destruction. The coupling of the water cluster vibrational THz modes to the bending mode of the soot particle (Fig. 21) is the first step in the decomposition of the latter and may be followed by pump-probe measurements.

![Fig. 21. Coupling of the water cluster vibrational THz modes to the bending mode of the soot particle, which is the first step in the decomposition of the latter.](image)

Stacey listed a few desired parameters of the THz FEL for gas-phase and cluster photochemical reaction studies.

- Optimal repetition rate:
  - Ion: Time of flight up to 50 µs (20 kHz)
  - Ion: Time of flight ~100 ns (10 MHz)
Spectroscopy requires X-ray energy resolution and tunability
- Ideally it should match the vibrational energy
- Ions: 500 meV OK
- Electrons: 50-100 meV might be OK

Intensities?
- Low density sample in gas phase
- THz: high absorption at resonance
- X-ray: \(10^{12}\) ph/sec

“(THz and) spectral X-ray imaging – technologies and applications” – Christer Fröjdh (Mid Sweden University)

Christer Fröjdh presented their research performed on X-ray detectors and their applications. At the Mid Sweden University they have a clean room designed for detector fabrication. They also characterize the detectors using radiation as well as with electrical methods, and they simulate their charge transport properties and interaction with radiation. Furthermore they work on the development of various X-ray imaging techniques such as spectral X-ray imaging, X-ray microscopy, and phase contrast imaging. Christer specifically talked about spectral X-ray imaging which is a powerful technique to identify materials in a complex object that is becoming very popular. It is based on the unique spectral absorption properties of each material and the difference in absorption at different photon energies is used for separation of the materials (Fig. 22).

Fig. 22. Sheets of Pd and Ag revealed by spectral X-ray imaging where difference in absorption at different photon energies is used for separation of the materials.
The Mid Sweden University is part of the MEDIPIX collaboration for development of hybrid pixel detectors for single photon counting processing, which is coordinated by CERN. The Timepix detector produced within this collaboration is currently in operation at the International Space Station and is evaluated as an option for radiation field monitors and personal dosimeters. MEDIPIX detectors are also utilized at ATLAS.

Christer concluded by proposing that the possibilities of the combination of THz and spectral imaging should be further explored.

References


Appendix

Workshop on the scientific opportunities of a THz FEL in Sweden
24-25 November 2014, AlbaNova University Centre Stockholm, Sweden

Program:

Monday, November 24

09:00 – 09:40 Registration and coffee

9:40 – 12:30 Chair: Vitaliy Goryashko (UU)

09:40 – 10:00 Mats Larsson (SU): Welcome and introduction
10:00 – 10:20 Tord Ekelöv (UU): The FREIA Laboratory and its future development
10:20 – 11:00 Wieland Schöllkopf (FHI): The new IR FEL facility at the Fritz Haber Institute in Berlin

11:00 – 11:30 Coffee

11:30 – 11:50 Peter Salén (SU): Design and scientific aims of the Swedish THz FEL
11:50 – 12:10 Vasyl Yatsyna (GU): THz FEL gas-phase action spectroscopy of molecular backbone motion
12:10 – 12:30 Serguei Cherednichenko (Chalmers): THz electronics

12:30 – 14:00 Lunch

14:00 – 17:30 Chair: Örjan Skeppstedt (SU)

14:00 – 14:40 Carlito Ponseca (LU): Charge carrier dynamics of the Perovskite solar cell probed by time-resolved THz spectroscopy
14:40 – 15:20 Stefano Bonetti (SU): Strong single-cycled THz fields
15:20 – 15:40 Corina Etz (UU, LTU): Spin dynamics simulations in the THz regime

15:40 – 16:10 Tea

16:10 – 16:50 Vanya Darakchieva (LiU): THz ellipsometry and the optical Hall effect
16:50 - 17:10 Dragos Dancila (UU): Terahertz for biomedical applications: activities in the microwave group.
17:10 – 17:30 Dag Hanstorp (GU): Spectroscopy of negative ions

17:30 – 19:00 Discussion headed by Peter van der Meulen (SU)

19:00 – 21:00 Conference dinner
Tuesday, November 25

08:50 – 10:30  Chair: Vitali Zhaunerchyk (GU)

08:50 – 09:30  Gergely Katona (GU): Quest for Fröhlich’s condensation in protein molecules
09:30 – 09:50  Olof Karis (UU): Short pulses or high energy resolution? At a crossroad for a THz FEL for spectroscopy
09:50 – 10:10  Alexander Soldatov (LTU): Synthesis and characterization of carbon-based nano-materials: what can be done using THz spectroscopy?

10:30 – 11:00  Coffee

11:00 – 12:30  Chair: Joseph Nordgren (UU)

11:00 – 11:40  Anders Nilsson (SU): Stimulating surface chemical reactions with THz pulses
11:40 – 12:00  Stacey Sörensen (LU): Time resolved spectroscopy with two-color pump-probe ionisation in molecules
12:00 – 12:20  Christer Fröjdh (MiUn): THz and spectral X-ray imaging – Technologies and applications
12:20 – 12:30  Mats Larsson (SU): Conclusions, final words and closure

12:30 – 14:00  Lunch