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APR 04 2000
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July 1999

National Synchrotron Light Source

Brookhaven National Laboratory
Operated by
Brookhaven Science Associates
Upton, NY 11973

Under Contract with the United States Department of Energy
Contract Number DE-AC02-98CH10886

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Two-color experiments combining the UV-Storage Ring Free Electron Laser and the SA5 IR beamline at Super-ACO

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ABSTRACT

The UV-storage ring Free Electron Laser (FEL) operating at Super-ACO is a tunable, coherent and intense (up to 300 mW) photon source in the near-UV range (300 - 350 nm). Besides, it has the unique feature to be synchronized in a one-to-one shot ratio with the Synchrotron Radiation (SR) at the high repetition rate of 8.32 MHz. This FEL + SR combination appears to be very powerful for the performance of pump-probe time-resolved and/or frequency-resolved experiments on the sub-ns and ns time-scales. In particular, there is a strong scientific case for the combination of the recently-commissioned SA5 Infra-Red Synchrotron Radiation beamline with the UV-FEL, for the performance of transient IR-absorption spectroscopy on FEL-excited samples with a Fourier-transform spectrometer coupled with a microscope allowing high spectral and spatial resolution. The principle and interest of the two-color combination altogether with the description of both the FEL and the SA5 IR beamline are presented. The first synchronization signal between the IR and the UV beams is shown. The correct spatial overlap between the UV (FEL) and the IR (SR) photon beams is demonstrated by monitoring via IR-spectro-microscopy the time evolution of a single mineral particule (kaolinite) under UV-FEL irradiation.

Keywords: Free Electron Laser, Synchrotron Radiation, Infra-red, Pump/probe experiments, Absorption spectroscopy, Infrared microscopy, Irradiation.

1. INTRODUCTION

As compared to the photons emitted by a "conventional" blackbody source, the Infra-red (IR) radiation emitted as Synchrotron Radiation (SR) by an electron in a storage ring at a bending magnet level, has two unique features : its time-structure and its brilliance. The latter one has been intensively used in the last decade to perform infrared micro-spectroscopic experiments in materials science¹ and in biology^{2,3} with high lateral resolution owing to the use of a microscope coupled with a Fourier-transform spectrometer. The first one has been also used for instance in the study of transient photoconductive decay of IR detectors materials, taking advantage of the fact that the SR in the IR is the only white pulsed source with short pulses in the sub-ns range, making it very suitable for time-resolved experiments.⁴ On the other side, a Storage Ring Free Electron Laser (SR-FEL) such as the one implemented on the Super-ACO storage Ring, is a unique coherent tunable and intense UV source, naturally synchronized with the SR, in a one-to-one shot ratio, leading to possible very interesting two-color pump/probe schemes. If one now considers the coupling between these two very complementary sources, one gets a unique tool for the performance of time-resolved, frequency-resolved and even spatially-resolved two-color UV+IR pump/probe experiments. Note

that to our knowledge, the Super-ACO set up is the first in the world to take advantage of such a combination, although the construction of a similar system is planned on the DUKE FEL.⁵

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The FEL (UV) + SR (IR) combination can be seen in the condensed matter as a very sharp analytical tool for the observation of structural and/or electronic motion induced by the UV-FEL irradiation on time-scales as short as a few 100's of ps. While in molecular sciences, the UV+IR combination might bring new insights on possible couplings between the electronic and nuclear motions respectively induced by UV and IR excitations.

In the next sections, we will present the potentialities and scientific cases brought about by the FEL(UV) + SR(IR) coupling, followed by the description of both sources : the UV SR-FEL of Super-ACO and the SA5 IR beamline. Then the first ever observed signal, showing the synchronization between a FEL and the SR (with the SR used in the IR range) altogether with results concerning the IR-probed time-resolved UV-irradiation of a single mineral particule (kaolinite), as a probe of the correct spatial overlap between the two beams, will be presented.

2. POTENTIALITIES OFFERED BY SR-FEL (UV) + SR (IR) COMBINATION

We will give here some general considerations on the main features relevant for the performance of pump/probe experiments using the combined FEL and SR sources,⁶ then the selected scientific case is reported for this FEL(UV) + SR (IR) combination.

UV-Storage Ring Free Electron Lasers (UV-SRFELs) happen to emit coherent light in the UV range and are based on storage rings ! These features are potentially extremely interesting in the sense that they open two important directions for applications, which are not directly possible to follow with the more and more challenging conventional lasers, as explicated below.

2.1 The emission in the UV

During the last years, with the increasing quality of the electron beam available on storage rings on which FELs are implemented, photons are getting available in the UV, for instance at Super-ACO since 1991 around 350 nm⁷ and very recently at 300 nm⁸, at UVSOR around 239 nm since 1996,⁹ at Duke around 217 nm,¹⁰ and more recently around 212 nm (the shortest wavelength !) at NIJI-4,¹¹ and very likely in the future in the Vacuum Ultra-Violet (VUV) range (below 180 nm).¹² This makes UV-SRFEL a very interesting and somehow unique tool for the performance of one-photon time-resolved and/or frequency-resolved experiments in photochemistry and photobiology since most of organic and inorganic molecules have their first electronically excited states lying in the 380-200 nm range. In the condensed matter, the use of UV light is also extremely interesting since it allows the electronic excitation of most systems including for instance wide Highest Occupied Molecular Orbital - Lowest Unoccupied Molecular Orbital (HOMO-LUMO) gap systems or wide-gap semi-conductors. In some cases, such an irradiation may lead to irreversible structural changes. The first UV-FEL to be used for a scientific application was the Super-ACO SR-FEL operating at 350 nm which allowed in 1994 the study of the time-resolved polarized fluorescence decay of a biological molecule, the NADH coenzyme. This experiment showed the feasibility of such an application and brought original results.¹³ In such experiments, beside the spectral range, one takes advantage of the linear polarization, the pulse-to-pulse stability and the high repetition rate of SRFELs which is very suitable for Time-Correlated Photon Counting-type experiments. Furthermore, one can set-up around SRFELs the same experimental environment as for table-top conventional lasers in terms of detection technique and sample preparation, such as a UHV chamber or a molecular beam chamber.

2.2 The natural synchronization with the synchrotron radiation

SRFEL and Synchrotron Radiation (SR) pulses share the same origin, the electron bunches travelling in the storage ring as depicted in Fig. 1, leading to a natural pulse-to-pulse synchronization between the two sources. Although several groups have been successful in the synchronization of mode-locked lasers with the SR (for a review see Ref. 6), including the synchronization of a visible Nd:YAG laser with the U4 IR beamline at NSLS for the performance of visible+IR pump/probe experiments on the ns-time-scale,^{4,14} these synchronization set-up, usually based on an electronic locking between the RF cavity of the ring and of the mode-locker RF can present some instabilities and drifts, with in addition a repetition rate different from the 1:1 ratio which can be a disadvantage for the exploration of long-time dynamics in time-resolved experiments. In addition, and this is the main point, if one considers the UV range covered by SRFELs, which is not accessible with a reasonable power by mode-locked conventional lasers, one can state that SR-FELs are a unique tool for the performance of pump/probe two-color experiments combining FEL and SR in order to use their very complementary features : high average power in the UV and spectral/temporal resolution for the former and wide (white) spectral range for the latter. All these features have been used for the performance of the first pump/probe experiment combining a UV-FEL with the SR in the X-UV range.¹⁵ This experiments was aimed to the study of the FEL-induced transient surface photovoltage at semi-conductor interfaces and gave new results on the the sub-ns photocarriers dynamics at the Si(111)2x1 interface.¹⁶

Figure 1. Layout of a storage ring producing Synchrotron Radiation (SR) from bending magnets and undulators, and on which is implemented a SR-FEL. The SR and FEL pulses are naturally synchronous as produced by the same electron bunches.

Two-color experiments fall into different categories :

(i) Frequency-resolved experiments, i.e. with a fixed pump-to-probe delay, in which one takes advantage of the synchronization for achieving a high temporal confinement of the two pulses, which strongly increases the two-photon pumping scheme efficiency via a short-living intermediate state. This increasing factor, determined by the temporal overlap of the two sources on the time-scale of the lifetime, as compared with the use of a cw laser in combination with the SR, depends of course on the duty factor of the SR source with typical values of 10^2 (SR second generation source) to 10^4 (SR third generation source) for the same laser average power.

(ii) Time-resolved experiments, in which the pump-to-probe delay is scanned or sampled in order to study the relaxation dynamics of the excited state, as it has been performed for decades in the visible with pulsed laser (see for instance Ref. 17). The probing photons sample the temporal decay curve of the excited state while keeping a cw detection scheme, since all the dynamical information resides in the pump-to-probe delay. The time range accessible for such time-resolved FEL + SR studies is usually limited on the short-time side by the SR pulse width ΔT_{SR} and on the long-time side by the repetition period of the SR pulses (T_{SR}). This temporal range, a few 100's ps-120 ns at Super-ACO for instance, corresponds to the dynamics timescale of

many relaxation processes either in the gas phase or in the condensed matter, such as predissociation, fluorescence, intra-molecular relaxation processes, electron/hole recombination or structural motion.

(iii) A combination of (i) and (ii) when for instance, for a series of given pump-to-probe delays, another variable of the experiments belonging to the frequency domain such as a photon or an electron energy is scanned, providing informations on a 2 D (time and energy) scale. Note that an another level of information can be added, with spatially-resolved data, as obtained with a microscope providing informations on a 3D scale with temporal, spectral and lateral resolution.

2.3 The scientific case for the UV+IR combination

With such unique features, associated with the intrinsic qualities of the SR such as its well-known stability, the FEL(UV-pump) + SR(IR-probe) combination exhibits high scientific opportunities in various applications, especially within the framework of transient Fourier-transform spectro-(micro)spectroscopy. In material sciences, the IR probe beam might be used to probe the transient photocarrier density on FEL-excited samples such as, for instance, wide gap semi-conductors, with possible applications in UV-photodetectors. In this sense, the UV-FEL can extend towards the UV range experiments that have been carried out in the visible with conventional lasers.⁴ IR probe beam can also be seen as an analytical tool able to probe the structural motion or modifications in real time of FEL-excited (-irradiated) systems. For instance, it is of particular interest to study the time-resolved changes of interfaces and thin films during UV-irradiation : photon-induced polymerization processes are known to occur as well as conformation changes. Such irreversible modifications, by modifying the nature of the chemical bonds, are easily tracked down by IR spectroscopy for different pump-to-probe delays and for different irradiating doses. In molecular physics and photochemistry, the UV + IR combination is potentially very fruitful since it implies both the nuclear and electronic motions and their possible couplings, which can be investigated by IR (pump) + UV (probe) experiments requiring high power IR lasers such as IR-FELs in order to pump vibrational overtones^{18,19} or, as here, in the UV (pump) + IR (probe) sequence. In the gas phase, the ns temporal confinement of the pump and probe pulses should allow the performance of experiments in a gas cell at pressure up to a few Torr in a collisionless regime. Then, the ro-vibrational energy content of molecular photofragments produced by FEL-induced photodissociation could be mapped out providing insights on the fragmentation dynamics. Reciprocally, the FEL could be used to produce, by laser-induced dissociation from a suitable molecular precursor, radicals whose ro-vibronic structure is interesting to study. Finally, the sub-ns dynamics of intra-molecular relaxation processes, due to electronic states coupling, such as inter-system coupling, could be investigated.

3. EXPERIMENTAL SET-UP

The experimental set-up includes the two photon sources, which will be described hereafter, that converge onto the same spot, which, in the present case, is the focus point of a synchrotron- IR microscope, at the sample level as depicted in Figure 2.

Figure 2. Schematics of the set-up used for the transient IR-absorption spectro-microscopy on FEL-excited sample

3.1 The SA5 IR-beamline

The Synchrotron Radiation is a unique source in the infrared region,²⁰ being about 1000 times brighter than standard thermal sources, polarized, and pulsed on the 100 picosecond timescale. It is also an absolute source, since the emitted power depends linearly on the electron beam current stored in the ring, which can be measured accurately. The instrumentation required to efficiently collect the IR emission from a bending magnet has been discussed in depth elsewhere.¹ The most important experimental details are of an engineering nature and are especially related with large opening angles of the synchrotron radiation, especially for long wavelengths collection. It should be noted that a novel infrared beamline has been built at Super-ACO, by Roy and co-workers,²¹ which collects light off-axis from an undulator, and also edge radiation from the upstream dipole.

We have built an IR beamline (SA5) on a bending magnet whose optical conception and performances are described elsewhere.²² Briefly, the 19° port allowed us the extraction of the SR with opening angles of 45 mrad horizontally and 18 mrad vertically. After reflection on a water-cooled Ni-coated copper mirror, the beam passes through two UHV-compatible KBr windows, and is made parallel (16 mm diameter) with two off-axis spherical mirrors and transported into an evacuated chamber towards the experimental room located 13 m downstream. The emerging beam, after passing through a KBr window which separates the evacuated chamber and the purged atmosphere, is directed onto the Michelson interferometer, used for Fourier-transform spectroscopy, and enters then the IR microscope (See Fig. 2).

The performances of this beamline show that a signal-to-noise obtained for 100 scans performed at 4 cm⁻¹ resolution, with an aperture of 3 x 3 microns, is a factor of about 1000 more important than for a blackbody source demonstrating the high brightness of the synchrotron source.²²

3.2 The Super-ACO UV SR-FEL

The principle of a Storage Ring FEL is well-established and can be understood as follows : the FEL oscillation starts from the well-known undulator fundamental radiation at the wavelength λ_0 , emitted by an ultra-relativistic bunch of electrons moving through the sinusoidal magnetic field of an undulator, given by :

$$\lambda_0 = \frac{\lambda_u}{2\gamma^2} \left(1 + \frac{K^2}{2} \right) \quad (1)$$

where λ_u is the period of the magnetic field, γ is the reduced energy of the electrons ($E[\text{MeV}]/0.511$) and $K = 0.934\lambda_u[\text{cm}]B_0[\text{T}]$ where B_0 is the peak magnetic field on axis. This emission is referred, in the context of a FEL, as the spontaneous emission from which the laser emission is building up. One clearly see from (1) the intrinsic tunability, via the tuning of the magnetic fields, one of the main interest of FELs. During their pathway throughout the undulator, and because of the interaction with the electromagnetic field associated with the SR, the electron bunches are submitted to an energy modulation which leads to an spatial micro-bunching at the wavelength λ_0 , leading to an increase of the coherence of the emitted SR. This radiation is stored in an optical cavity, composed of two spherical mirrors, whose length is chosen so that the round-trip time for the photon in the cavity corresponds to the inter-bunch period. If now there is a proper longitudinal and transverse overlap between the photon pulses trapped inside the cavity and the electron bunches circulating through the undulator, an energy exchange can occur, via the Lorentz interaction, between the photon and the electron at the expense of the latter and in favor of the former. This leads to an exponential laser amplification, which at some point is limited by different saturation mechanisms leading to a saturated gain equal to the losses of the cavity. One of the main challenge at Super-ACO, for which the insertion length is rather short (~ 3 m) is to extract most of the possible gain G_0 (typically 2 %) while minimizing the losses L (by absorption, scattering and transmission) on the high-reflecting multi-dielectric mirrors of the cavity. The FEL behavior, as for any other kind of laser, is determined by the threshold condition $G_0 > L$. For instance, owing to a recent increase of the gain, it has been possible to increase the transmission of the mirrors, producing an enhancement of the available power up to 300 mW.²³ Besides, the threshold condition, together with the electron beam dynamics, also governs the longitudinal dynamics of the laser including the extremely important issue of the macro-temporal and micro-temporal stability. The main updated characteristics of the Super-ACO FEL are listed in Table 1.

The output power is extracted from the cavity by transmission (about 0.1 %) through the multi-layer mirrors and is then carried out towards one of the different application set-up by simple high-reflecting plane mirrors owing to its excellent transverse diffraction-limited properties. In the present case, the FEL beam is conveyed towards the IR spectro-microscope hutch located a few meters away. Finally the beam is focussed with a 20 cm focal length plano-convex lens onto the sample which is hit at a 80° incidence angle, as depicted in Fig. 2.

Table 1. Main characteristics of the Super-ACO FEL.

Parameter	Value	Remarks
Ring Energy [MeV]	800	Highest ring energy for the operation of a SR-FEL and nominal energy of the Super-ACO storage ring
Current for FEL operation [A]	100 - 20	Within two bunches
FEL lifetime [h]	3 - 9	Depending on the use of a 500 MHz harmonic cavity on the ring
Spectral range covered [nm]	430 - 300 ^a	With different set of cavity mirrors
Tunability range [nm]	10 to 20	Limited by the reflecting bandwidth of the multi-dielectric mirrors
Relative Spectral width [%]	10 ⁻⁴	A factor 1.2 - 4 above the Fourier limit
Maximum output power [mW]	300 mW	Highest available power on a SR-FEL
Repetition rate [MHz]	8.32	The same as the Synchrotron Radiation
Pulse width FWHM [ps]	15 - 60 ps	A factor 1.2 - 4 above the Fourier limit
FEL/SR jitter [ps]	< 10	Owing to the longitudinal feedback on the FEL ^b
Intensity fluctuations [%]	< 1	Over an hour, owing to the longitudinal feedback on the FEL ^b
Polarisation	linear horizontal	as the SR collected in the orbit plane
Transverse mode	TEM ₀₀	The transverse properties are diffraction-limited

^aSee Ref. 8^bSee Ref. 24

4. FIRST RESULTS

4.1 The FEL / SR synchronization

One of the main issue one has to face when dealing with time-resolved two-photon experiments is related to the pump-to-probe synchronization. In our experimental set-up, and this is a major advantage of the FEL+SR combination, the synchronization is intrinsic, so that the only two parameters which are to be kept under control are : (i) the setting and the measurement of the actual delay between the pump and the probe; (ii) the possible jitter between the pump and the probe.

On its way to the IR-micro-spectrometer, the FEL beam is directed towards a computer-controlled optical delay line, which has a total delay range of 8 ns owing to a reflecting corner-cube moving onto a 1.2 m-long translation stage. In our set-up, the accessible delay range is + 3.5 ns down to - 4.5 ns : a positive delay corresponds to a situation where the pump (FEL) pulse impinges onto the sample before the probe (SR) pulse. Note that because of the 120 ns interpulse period, a negative delay, for instance -4 ns, corresponds to a +116 ns pump-to-probe delay with respect to the next SR pulse. In order to determine the "zero delay" reference and to show the delay tunability, we have set a Silicon pin photodiode at the sample location, at the focal point of the microscope, and with the Michelson interferometer motion frozen. We have then recorded the signal, after amplification, with a 500 MHz digital oscilloscope. The resulting signal is shown on Figure 3 for three different settings of the optical delay line, clearly demonstrating the tunability of the pump-to-probe delay, with an absolute precision in the range of ± 100 ps.

The overall temporal jitter between the FEL and the SR is an important issue, especially in the case of short-living excited states. Such a jitter is related on one hand to the SR pulse-to-pulse instability, which arises from the jittering of the electrons bunches and on the other hand to the FEL/SR pulse-to-pulse synchronization, which originates from the jittering of the FEL micropulses with respect to electron longitudinal distribution. Owing to the good longitudinal stability of the electron beam and to a

longitudinal feedback on the laser,²⁴ the overall jitter is limited at Super-ACO to less than 10 ps. The overall temporal resolution is then not limited by the jitter, but rather by the temporal cross correlation of the FEL (typically 15 - 50 ps) and SR pulses (typically 200 - 400 ps FWHM). This gives a typical overall resolution mostly dominated by the SR width in the 200 - 400 ps temporal range. In addition, one has to take into account the slippage of one pulse with respect to the other due to the Michelson interferometer arm motion during the recording of a spectra composed of many scans. The motion range depends of course on the required resolution. Considering typical resolutions of 4 cm^{-1} (study of condensed matter) and 0.5 cm^{-1} (study in the gas phases), the motion of the moving mirror is respectively 0.25 cm and 2 cm. This corresponds to an additional broadening of 8 and 66 ps respectively. This slippage effect clearly sets a lower limit for the accessible temporal resolution of such an experiment performed with ps photon sources based on third generation storage rings. In our case, considering the SR pulsewidth, this effect is negligible.

Figure 3. FEL and SR pulses signal as recorded with a pin Silicon photodiode for 3 different settings of the optical delay line : (a) +2.4 ns delay (FEL before the SR); (b) zero delay (perfect temporal overlap); (c) - 2.5 ns delay (FEL after the SR). The precision in the temporal calibration is of ± 100 ps.

4.2 UV Irradiation probed by IR-microspectroscopy

One of the first experiments that has been carried out concerns the UV-irradiation effect on a single particle, probed by the synchrotron IR source. Despite the irreversible character of the irradiation, this experiment helps qualifying the concomitant effect of the pump-probe study on a particle of micron size, as a probe of the satisfactory spatial overlap of the two beams.

Figure 4. Optical image of the kaolinite single particle that has been time-evolved studied by synchrotron IR spectroscopy during UV-FEL irradiation. The full horizontal width of the image is 25 μm .

Figure 4 shows the image of the probed kaolinite particle. This mineral belongs to a major class of sedimentary reservoir rocks which are mainly composed of quartz grains. It's a layered compound composed of tetrahedral (SiO_4) and octahedral (AlO_6) sheets.²⁵ The infrared spectra of such compounds are well understood.²⁶

Figure 5. Synchrotron IR spectra of the kaolinite particle shown on Figure 4 after various irradiation time (in minutes). The arrows indicates the modified vibrational bands (see text).

In Figure 5 is displayed the resulting IR spectra, after various irradiation time. The spectra are displayed in the two frequency regions of interest. Between 3500 and 3800 cm^{-1} , the different types of OH- terminations exhibits 4 bands at 3622, 3655, 3670 and 3700 cm^{-1} , assigned to "inner" OH for the first three, and to inner-surface OH groups for the latter. The outer OH, located at 3700 cm^{-1} , has been found to be the most sensitive to wetting processes.²⁷ It appears clearly that the band assigned to the stretching motion of the "external OH" is strongly affected by the UV irradiation, as it loses intensity during extended irradiation time. Meanwhile, the "internal" OH remains unaffected. The bands appearing in the 800-1200 cm^{-1} frequency region, have several origins: Al-OH deformations (850-950 cm^{-1}) and silicate as well as Si-OH deformations between 950 and 1200 cm^{-1} . In Fig 5, it can be seen that the broad feature lying around 1050 cm^{-1} is also affected by the UV irradiation. This is tentatively assigned to a deformation mode of an external Si-OH species.

5. CONCLUSIONS

With the numerous improvements of its performances in the last years, the Super-ACO UV FEL has reached a stage of maturity, which allows the continuation of performance of experiments in combination with the synchronous SR, a scientific program initiated a few years ago. In the very broad spectral range covered by the SR, the IR part appears to be very interesting for the coupling with the UV, as a time-resolved probe of FEL-induced excitation and/or irradiation. A dedicated synchrotron IR beamline (SA5) has been built, which shows very good performances in terms of brightness. We have shown here the first signal corresponding to the synchronization, on the sub-ns timescale, of the FEL with the SR in the IR as emitted from SA5 beamline. Moreover, as a first demonstration of the capabilities of such an experimental set-up, and as a probe of the spatial overlap between the pump and probe beams, we have recorded the time-evolved IR spectra of one single (micron-size) kaolinite particle during UV irradiation. Spectroscopical informations indicates that the external OH groups are strongly modified by the UV light, tuned at 350 nm. This kind of experiments, which proof-of-principle has been demonstrated here, should be performed in the near future on molecules adsorbed on films as well as in the gas phase with dynamics lying in the ns and sub-ns timescales.

ACKNOWLEDGMENTS

We would like to thank Alain Delboulbé, Michel Tanguy and Jean-Pierre Marx for their unvaluable contribution in the design and construction of the SA5 IR beamline, and Thierry Guillou for the setting-up of the FEL transport optics, as well as the technical staff of Lure for operating the Super-ACO storage ring. Jean-Louis Bantignies is acknowledged for providing clays samples.

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