ELSEVIER

Nuclear Instruments and Methods in Physics Research A 483 (2002) 560–564

NUCLEAR INSTRUMENTS & METHODS IN PHYSICS RESEARCH Section A

www.elsevier.com/locate/nima

Commissioning of a UV/time-resolved-FTIR beamline at the Duke FEL laboratory

M. Shane Hutson[a], Richard A. Palmer[b], Ming-Shien Chang[a], Angela Gillikin[b], Vladimir Litvinenko[a], Glenn Edwards[a,*]

[a] *Duke University Free Electron Laser Laboratory, P.O. Box 90319, Durham, NC 27708, USA*
[b] *Chemistry Department, Duke University, Durham, NC 27708, USA*

Abstract

We describe the commissioning of a novel two-color beamline at the Duke Free Electron Laser Laboratory, designed to perform time-resolved FTIR spectroscopy in a pump-probe scheme with sub-nanosecond resolution to measure dynamical processes with durations as long as 10 ns. The UV pump pulses are produced by the tunable (193–700 nm) output of the OK-4 Storage-Ring FEL. The broadband, infrared probe pulses are generated as synchrotron radiation in a bending magnet downstream of the OK-4 wiggler. The repetition rate of the light source (2.79 MHz) is ideal for operating the interferometer in the rapid-scan, asynchronous sampling mode. An investigation of DNA photolyase is proposed.

PACS: 78.47.+p; 78.30.Jw; 41.60.Cr; 41.60.Ap

Keywords: Storage-ring FEL; Time-resolved FTIR

1. Introduction

A novel, two-color beamline has been commissioned at the Duke Free Electron Laser Lab to perform time-resolved UV-pump/IR-probe measurements. The pump beam is supplied by the output of the OK-4 UV FEL operating on the Duke storage ring. It is capable of lasing throughout the visible spectrum and deep into the ultraviolet, to wavelengths as short as 193 nm. The broadband, infrared probe pulses are generated as synchrotron radiation in the downstream bending magnet. As the same bunch of electrons emits both pulses, the timing between the pump and probe is essentially jitter-free and the attainable time-resolution is thus limited by the pulse-widths. The capability to excite systems with tunable ultraviolet radiation and then probe the relaxation processes with broadband, mid-infrared radiation over durations as long as 10 ns with a time resolution on the order of 100 ps is unique. This opens the door to the study of photochemical and photobiological systems not previously accessible to time-resolved infrared spectroscopy.

2. Asynchronous sampling

Step-scan Fourier-transform-infrared (FTIR) spectroscopy in the asynchronous sampling mode

*Corresponding author. Tel.: +1-919-660-2674; fax: +1-919-660-2671.

E-mail address: edwards@fel.duke.edu (G. Edwards).

0168-9002/02/$ - see front matter
PII: S0168-9002(02)00382-0

[1] enables subnanosecond resolution for the broadband infrared probe. In this application of asynchronous sampling, the broadband IR source probes a sample material that is resonantly pumped in the UV as summarized in Fig. 1. The IR source can be viewed as a distribution of Fourier components. Panel A represents the interferogram for a single Fourier component, i.e. first modulated in intensity by the Michelson interferometer, then passing through an absorbing sample onto the detector. Panel B represents the perturbation to the probe signal due to repetitively pulsing with the UV pump. In Panel C, a pulsed IR probe is synchronized with the UV pump to interrogate the relaxation of the excited state due to UV absorption, where the traces of panels A and B are included for reference. Since neither the pump nor the probe pulses are synchronized to the scanning of the Michelson interferometer, over time all phases of the modulated intensity are measured. As shown in Panel D, the discrete interferogram of Panel C has been converted into a continuous interferogram with a low pass electronic filter. Note the repetition rate must exceed the highest Fourier frequency by a factor of two (40 kHz in our case) to avoid a sampling artefact (aliasing). Fourier transforming the sum of interferograms for all of the Fourier components results in a single-beam spectrum, which can be ratioed against the no-excitation spectrum to generate a differential absorption spectrum. By systematically varying the delay between pump and probe, the overall relaxation processes are mapped out. In the single bunch mode, the synchrotron radiation pulse repetition rate of the Duke storage ring is 2.79 MHz, well in excess of that required for asynchronous sampling FTIR.

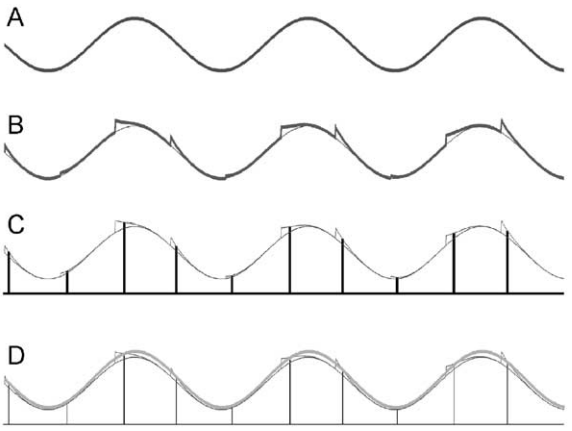

Fig. 1. Schematic diagram of the asynchronous sampling method for time-resolved FTIR. Intensity as a function of mirror retardation, or equivalently, time.

3. Commissioning of the UV-Pump/IR-Probe beamline

The Duke storage ring was built with the dedicated purpose of providing electrons for the OK-4 FEL, which has been operational since 1996. More recently, water-cooled copper disks were installed in the corners of the ring to absorb the X-ray component of the synchrotron radiation from the bending magnets. In order to extract the optical (UV, visible and IR) components of the synchrotron radiation, optical flats were machined onto these copper disks. The size and placement of these flats, along with the space restrictions in the dipole bending magnets, determine the acceptance angles for capture of the synchrotron radiation at 57 mrad horizontally and 14 mrad vertically. While the vertical acceptance angle severely restricts the collection of far-infrared ($<500\,\mathrm{cm}^{-1}$) light, the theoretical extraction of mid-IR radiation is comparable to IR beamlines at NSLS [2,3].

We have designed, installed and commissioned an optical system to collect the synchrotron radiation (SR) reflected downward from the copper flat in the SE corner of the Duke storage ring as shown in Fig. 2. A gold-coated plane mirror located 20 cm below the copper flat reflects the SR towards a 6″ diameter, $f/6$ spherical mirror. The spherical mirror directs the SR back past this plane mirror and focuses the light through a CaF_2 window that separates the ultra-high vacuum (10^{-10} Torr) of the storage ring from the remainder of the beamline (10^{-7} Torr). The SR emerging from the storage ring vacuum chamber is then collimated by a 90° off-axis parabolic mirror ($f_{\mathrm{eff}} = 7.5''$). The collimated SR is then directed 20 m down the beamline by a pair of plane steering mirrors. The SR is brought out of the beamline

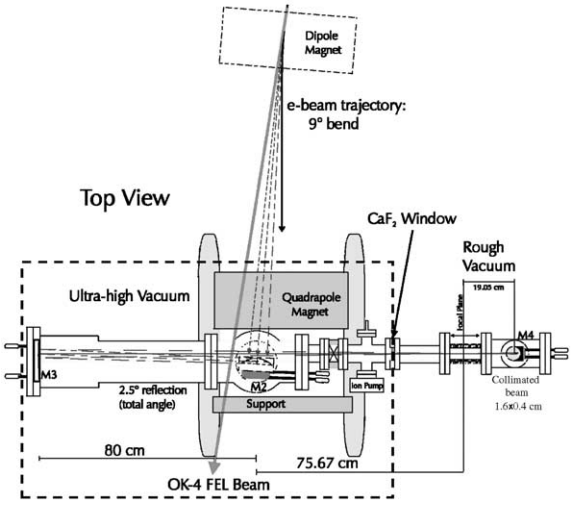

Fig. 2. Layout of the collection optics for the synchrotron beamline.

vacuum system at the endstation through a second CaF_2 window. At this point, the SR encompasses wavelengths from $\sim$450 nm to 9 μm, limited at long wavelengths by the CaF_2 windows.

Once at the endstation, the SR is directed through a N_2 purged path to the level of the optical table by a steering mirror and focused by a 90° off-axis parabolic mirror ($f_{\text{eff}} = 5.5''$). The focal point serves as an effective point source for a Bruker IFS-66v FTIR spectrometer. We have measured the SR power with the FTIR and compared it to theoretical expectations. Due to the effects of beam divergence over the 20 m between the collimating mirror and the endstation and reflection losses from each mirror and window, approximately 40% of the theoretically available SR power is delivered to the FTIR. Using a collimating mirror with a longer effective focal length could reduce the divergence losses. However, the mirror currently in use has the longest f_{eff} available in a diamond-turned 90° off-axis paraboloid.

The ring current and SR power decrease exponentially during the course of a single injection cycle of the storage ring (about 2 h). This creates a drift problem for measuring pump-probe difference spectra, as the low light levels require 5 min of signal averaging to achieve a SNR of 1000 (i.e. the ability to detect pump-on versus pump-off difference signals of 0.001 absorbance units). Consequently, we have installed an electronic shutter to measure the pump-on and pump-off spectra as an interleaved set, avoiding the drift problem.

To perform the two-color pump-probe experiment we must also deliver the coherent UV output of the OK-4 free electron laser to the endstation. This is accomplished by extracting the UV light from its evacuated beamline that parallels the SR beamline. Once the UV-pump pulse arrives at the optical table, it is directed through a delay line and then focused onto the sample in the spectrometer. Currently, we can delay the relative arrival times of the UV-pump and SR-probe pulses at the sample by >10 ns, where the intensities of the two pulses have been shown to remain constant within 5% without any realignment of the optics as the optical path length is varied.

A Hamamatsu streak camera was used to measure the pulsewidth of the SR. The results of this measurement show that the SR pulsewidth increases as the single-bunch current in the ring is increased, up to 360 ps at 10 mA. When these measurements are compared to previous pulsewidth measurements at mostly lower currents (the two sets of measurements overlap near 3 mA), the pulsewidths are now a factor of 2 longer than they have been in the past [4]. By optimising the electron orbit in the ring, this factor of 2 should be recovered. The lasing pulsewidths of the OK-4 will be a factor of 2–5$\times$ smaller than the SR pulsewidths.

4. Biophysical application

One of our near-term objectives is to investigate unresolved questions concerning the enzymatic mechanism of DNA photolyase. This protein binds to UV-induced lesions in DNA (specifically pyrimidine dimers) and then catalyses the cleavage of the pyrimidine dimers when exposed to blue light [5]. All evidence points to the involvement of photo-induced electron transfer in the catalytic mechanism. However, time-resolved absorption spectroscopy in the UV-visible spectral region

has not been able to identify the nature of the intermediates in this process [6]. Once the photoexcitation of the bound flavin chromophore was quenched, an unidentified intermediate arose within 2 ns after the flash ($\lambda_{max} = 400$ nm). The remaining steps were silent in the visible spectral region. By extending the accessible spectral range to include the near and mid-IR, the electron transfer events in this photocycle should no longer remain silent or unidentified. Vibrational frequencies in the mid-IR are extremely sensitive to changes in the spatial distribution of electron density. By simultaneously probing a broad range of mid-IR frequencies, we will be able to monitor the catalytic involvement of the flavin chromophore, residues of the enzyme and the DNA bases of the pyrimidine dimer. In addition, the time-resolved FTIR spectra will contain information regarding conformational changes in the protein and DNA backbones that accompany the photocatalytic cycle.

It is instructive to estimate the minimum power necessary for the proposed investigation of DNA photolyase. Consider an optimized time-resolved pump-probe experiment with parameters matching the Duke OK-4 FEL and synchrotron beamline. Using the synchrotron radiation as the probe with a single electron bunch in the storage ring ($F_{rep} = 2.79$ MHz), our sensitivity is limited to $\Delta A_{IR,min} = 0.001$. For a strong vibrational band, e.g. an amide or carboxylate, we have $\varepsilon_{IR} = 600\,M^{-1}\,cm^{-1}$. If we optimize the optical system to provide a diffraction limited spot in the Bruker IFS-66v sample compartment then $w = 50\,\mu m$. The required power decreases as the wavelength increases, so we will calculate the power necessary at the upper end of the OK-4 tuning range, $\lambda = 400$ nm. Furthermore, we presume the sample absorbs all of the available light (actual samples will only absorb between 50% and 90% of the incident light). Under these conditions, we find a threshold power of 109 mW (i.e. 40 nJ per pulse at 2.79 MHz). Several hundred milliwatts on the sample is a judicious target threshold given this idealized assessment. It should be noted that non-biological systems with more intense absorption place less power demands on the light sources. More specifically, $600\,M^{-1}\,cm^{-1}$ is about as strong as vibrational bands get. Alternatively, electronic transitions can exhibit molar absorbtivities $100\times$ greater. Indeed the semiconductor HgCdTe served as the experimental system for the commissioning of the NSLS time-resolved IR beamline [2,3].

4 mW of average power at 240 nm was measured at the endstation, produced by a single electron bunch at 450 MeV and a current of $\sim$11 mA. Vertical instabilities prevented more current in a single bunch. Currently we are upgrading the storage ring, promising to increase the single-bunch current to 20 mA and the electron energy to 1.2 GeV. There is a trade-off, however, between laser power and the SR pulsewidth, the limiting factor in time resolution.

5. Concluding remarks

We have commissioned the pump-probe beamline, characterizing both light sources. We have proposed initial applications experiments that utilize the beamline. The synchrotron radiation power level is $\sim 200\,\mu W$ between 2–9 μm, where we have maintained the intrinsic brightness of SR throughout the beamline. The SR pulsewidth is 200–400 ps (FWHM) depending upon the amount of current stored in the electron bunch. The coherent radiation from the OK-4 that is used to excite the samples has a pulsewidth 2–5$\times$ shorter than the SR and approaches 5 mW of average power for single-bunch operation of the storage ring. Upon completion of the current storage ring upgrade, we will pursue parallel tracks. While confirming the beamline's capabilities with experiments on semiconductor samples, we also will continue to increase the sensitivity of our IR measurements and increase the power levels available in the UV to enable the experiments for which the beamline was originally designed.

Acknowledgements

This research has been supported by the DoD MFEL program as administered by the AFOSR through contract number F49620-00-1-0370 and

by the ONR through contract number N00014-99-1-0891.

References

[1] K. Masutani, H. Sugisawa, A. Yokota, Y. Furukawa, M. Tasumi, Appl. Spectrosc. 46 (1992) 560.
[2] G.L. Carr, R.P.S.M. Lobo, C.J. Hirschmugl, J. LaVeigne, D.H. Reitze, D.B. Tanner, Proc. SPIE 3153 (1997) 80.
[3] R.P.S.M. Lobo, J. LaVeigne, D.H. Reitze, D.B. Tanner, G.L. Carr, Rev. Sci. Instr. 70 (1999) 2899.
[4] A.H. Lumpkin, B.X. Yang, V. Litvinenko, B. Burnham, S. Park, P. Wang, Y. Wu, Nucl. Instr. and Meth. A 407 (1998) 338.
[5] A. Sancar, Biochemistry 33 (1994) 2.
[6] T. Okamura, A. Sancar, P.F. Heelis, T.P. Begley, Y. Hirata, N. Mataga, J. Am. Chem. Soc. 113 (1991) 3143.