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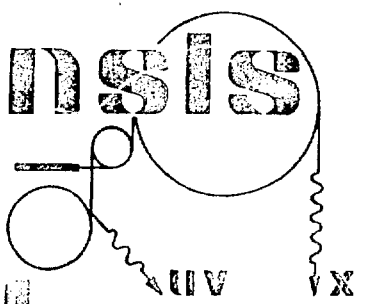

REPORT FROM THE NSLS WORKSHOP

Sources and Applications of High Intensity UV-VUV Light

Edited by E. D. Johnson and J. B. Hastings

22-23 January 1990

NATIONAL SYNCHROTRON LIGHT SOURCE

BROOKHAVEN NATIONAL LABORATORY
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Informal Report

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EXECUTIVE SUMMARY

A workshop was held to evaluate sources and applications of high intensity, ultra violet (UV) radiation for biological, chemical, and materials sciences. The proposed sources are a UV free electron laser (FEL) driven by a high brightness linac and undulators in long, straight sections of a specially designed low energy (400 MeV) storage ring. These two distinct types of sources will provide a broad range of scientific opportunities that were discussed in detail during the workshop.

The next generation radiation sources will be FEL's that can provide performance beyond 'conventional' lasers. The UV-FEL will provide a tunable source from the visible (5000Å) down to 1000Å, with an output energy in 2×10^{-4} bandwidth of 1 mJ per 6 psec pulse, and an average output power of 1-10 watts. Below 2000Å, this peak power far exceeds what can be expected from conventional lasers in the near future. The UV-FEL design specifications have been motivated by the realization that their achievement will open up new opportunities in photochemistry, with applications to processes important in combustion and atmospheric reactions.

Under construction today are the 'third generation' photon sources, the 1 GeV Advanced Light Source (ALS) at LBL and the 7 GeV Advanced Photon Source (APS) at Argonne. Both address the need for undulator based sources. They efficiently span the soft x-ray to hard x-ray range, however even the ALS, struggles in the energy range 5-30 eV where the elimination of harmonic contamination of the primary energy is crucial to new science. This concern is addressed by the low energy ring.

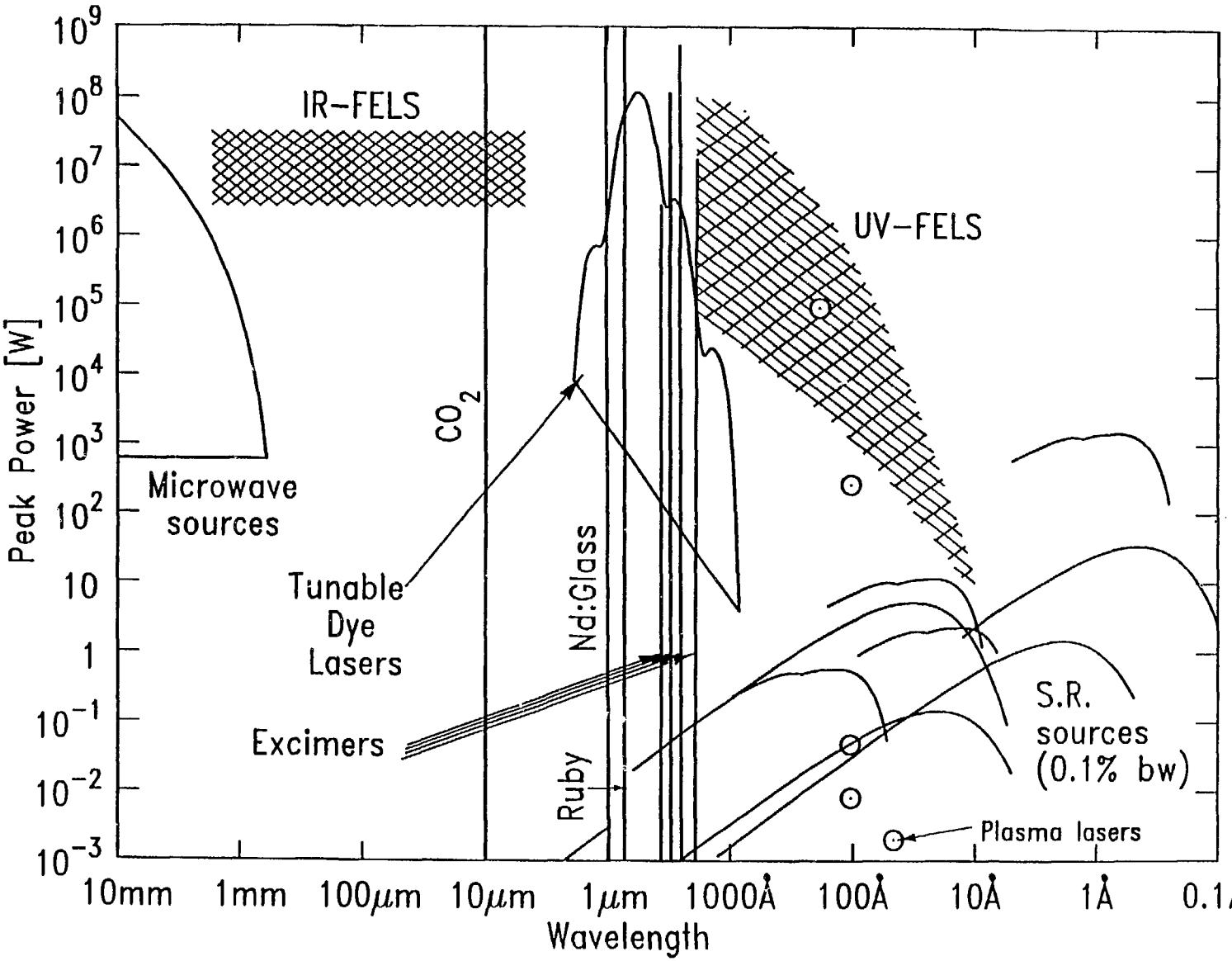
The undulators on the 400 MeV storage ring are designed to provide 10^{16} photons/sec in a 0.1% bandwidth in the energy range 5-30 eV. The low energy of the storage ring allows the generation of the soft photons using an undulator with short period and small strength parameter $K \leq 1$, reducing the intensity of the higher undulator harmonics. These undulator sources are ideal for the study of the electronic structure of materials utilizing high resolution angle resolved photoemission, with an achievable energy resolution of 10 meV and a momentum resolution of $0.01 Å^{-1}$.

The NSLS at Brookhaven can provide several unique features in the development of both the sources and applications. Early development of the scientific program envisioned for the new facility can be begun at the NSLS by building a new beamline designed for 5-30 eV photons utilizing the U13 undulator on the VUV Ring. Moreover, there is a great deal of on-going R&D being carried out at BNL relevant to the development of the UV-FEL and the low energy storage ring. A high brightness laser cathode electron gun is being developed at the Accelerator Test Facility (ATF) with characteristics suitable for the UV-FEL. Also, an FEL oscillator operating in the visible is under development at the ATF, utilizing a 50 MeV LINAC and a novel 8.8mm period superconducting wiggler magnet. Touschek scattering and ion trapping effects, which are of key importance to the performance of the 400 MeV storage ring, are subjects of studies

on the NSLS VUV Ring and on the Phase I 200 MeV storage ring to be built as part of the Superconducting X-ray Lithography Source (SXLS) Project.

It is useful to compare peak output power of the proposed UV-FEL with that of conventional and synchrotron-based sources. Fig. 1 summarizes the peak output power for a variety of radiation sources in a wide wavelength range from microwaves to hard x-rays. Included are conventional microwave sources, lasers, plasma lasers, second-generation (NSLS) and third-generation (ALS, APS) synchrotron sources, and the range of possible infrared and ultraviolet free electron lasers (FELs). A relative photon energy bandwidth ($\Delta E/E$) of 10^{-3} was used to calculate peak power for the synchrotron sources, although a monochromator is needed to achieve this bandwidth. The bandwidths used for the other sources are typical values for each source, e.g., 10^{-3} to 10^{-4} for FELs and much narrower for lasers. The data for microwave, laser, plasma, and FEL sources is taken from Science 250, 88 (1990), except the most powerful plasma source, which is taken from Science 247, 1553 (1990). The IR and UV FELs occupy regions of the peak power spectrum which are not presently reachable by the other types of radiation sources. The UV-FEL proposed here will produce approximately 10^8 Watts peak power in the 1000Å wavelength range, placing it at the top of the cross-hatched UV-FEL region.

Summarizing the contributions to the workshop, it is clear that the development of FEL sources at shorter wavelengths is truly the next generation light sources. The energy range 5-30 eV is possible with today's technology. The breadth of scientific opportunities is also unique in this energy range covering the chemical, materials, and biological sciences. Parallel development of undulator based sources on a low energy ring is clearly justified.



ORGANIZATION

The workshop was held over a two-day period, with talks on a broad range of subjects as can be seen from the list of speakers. After the workshop, summaries were compiled, and sample signal calculations solicited to try to provide an upper bound on the requirements of a source. Conclusions based upon this information are given in the last section of this report.

List of Speakers

Biological Applications:	
Raman Spectroscopy	J. Friedman
Time Resolved Fluorescence	W.R. Laws and J.B.A. Ross
DNA Damage and Repair	J.C. Sutherland & B.M. Sutherland
Chemical Applications:	
Frontiers in VUV Chemistry	W. Chupka
VUV Chemistry	E. Grant
Uses of MOPA in UV Chemistry	M. White
Solid State Physics:	
Time Domain Non-Linear Optics	E.W. Plummer
High Resolution Photoemission	E. Jensen
Non Linear Optical Phenomena in the Soft X-ray range	J. Bokor
Source Physics:	
UV VUV Generation with Lasers	L. DiMauro
FEL Physics	S. Krinsky
Rings and Undulators	J. Murphy
Parameters of a UV FEL	Li Hua Yu
Linacs for FEL's	I. Ben-Zvi
Present Status of FEL Development for the UV/VUV	B. Newman

Reports from Sub-fields

Accelerator-based Sources of VUV Radiation	S. Krinsky
Low Energy Photons in Solid State Research	P.D. Johnson
Primary Photochemistry with a VUV-FEL	M.G. White, W.A. Chupka, and E.R. Grant
Biological Applications of VUV Radiation	J.C. Sutherland

ACCELERATOR BASED SOURCES OF UV RADIATION

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This workshop addresses the development of a facility providing photon sources in the energy range 3-30 eV with unique capabilities for use in research in the Material, Chemical, and Life Sciences. The facility is comprised of an ultraviolet free electron laser (UV-FEL) driven by a high brightness 250 MeV Linac, and undulators situated in the long straight sections of a specifically designed 400 MeV storage ring. Utilizing recirculation, the Linac can provide full energy injection into the storage ring. Although not the subject of this workshop, infrared FEL and synchrotron radiation sources will also be provided in a straightforward manner.

The UV-FEL operates from the visible down to 1000Å, with an output energy in 2×10^{-4} bandwidth of 1 mJ per 6 psec pulse, with an average output power of 1-10 watts. These design specifications have been motivated by the realization that their achievement would open up new opportunities in photochemistry and nonlinear optics. The FEL design is based upon requirements on the laser cathode electron gun that are presently within the state of the art: normalized rms emittance 6×10^{-6} πm-rad for 100 Amperes peak current. Expected progress in electron gun development will further benefit the FEL design. Two possibilities for the 250 MeV Linac are under consideration: a SLAC type s-band structure, and a 500 MHz superconducting recirculating Linac. The SLAC type structure is less expensive, simpler, and more compact; however, the superconducting design offers the advantages of cw operation, improved energy spread and stability, and reduced transverse impedance. A beam recirculation scheme with a total of 3 passes could reduce the cost of the superconducting accelerator.

The wiggler magnet for the UV-FEL is about 21 m in length. An initial 11 m exponential gain section with wiggler period 1.75 cm and magnet gap 4 mm is followed by a short dispersion section to bunch the electron beam, and then a 10 m tapered section providing 1.2% transfer efficiency from electron beam power (250 MV x 100 Amp = 25 GW) to output radiation power (0.3 GW).

Three approaches to the operation of the UV-FEL are being considered. At present, most of the analysis is based upon using a dye laser as a seed to the FEL amplifier. Using harmonic generation from the output of a dye laser, a seed pulse with wavelength as short as 1000Å and energy between 4.0 μJ and 40 μJ can be generated and sent into the exponential growth section of the FEL. The advantage of this approach is that the final FEL output frequency can be as stable as the seed. An alternate scheme is to use a visible or infrared laser as the seed, and an initial section of the FEL as a resonant frequency tripling device, generating radiation and strong bunching of the electron beam at the third harmonic (as suggested by Bonifacio, et al.). The electron beam, bunched at the third harmonic, is then sent into the exponential growth section resonant with the third harmonic to be amplified. The advantage of

proceeding in this manner is that a laser more easily tunable than a dye laser can be used as the seed, e.g., a titanium sapphire laser. Detailed calculations to check the feasibility of this approach are to be carried out. The third option is to utilize a master oscillator power amplifier configuration (MOPA). In this case, an initial FEL oscillator situated in an resonant cavity is followed by an FEL amplifier. The oscillator can provide trains of micropulses (each with 8 μJ energy) to the power amplifier. The MOPA can provide high average power even with a conventional (room temperature) Linac. The requirement on the electron beam energy stability is more stringent than the previously mentioned approaches. Also, there is the technical difficulty of developing a fast and stable kicker to switch alternating bunches separately into the oscillator and the power amplifier.

The 400 MeV storage ring has a circumference of 51 m with 10 m straight sections for undulators. The undulators are designed to provide 10^{16} photons/sec in a 0.1% bandwidth in the energy range 5-30 eV. The low energy of the storage ring allows the generation of the soft photons using an undulator with short period and strength parameter $K \leq 1$. The storage ring operating current is 1 Ampere, and the electron beam lifetime of two hours is set by the intrabunch (Touschek) scattering. Since the Touschek lifetime is proportional to the bunch volume, the ring is run at full coupling with electron beam emittance $\epsilon_x = \epsilon_y = 10^{-7}$ πm-rad. The fundamental RF frequency is 52 MHz, and a 4th harmonic cavity is used to lengthen the bunch. Clearing electrodes are provided to prevent deleterious effects due to ion trapping.

There is a great deal of on-going R&D being carried out at BNL relevant to the development of the UV-FEL and the low energy storage ring. A high brightness laser cathode electron gun is being developed at the Accelerator Test Facility (ATF) for use in a 50 MeV Linac. Moreover, an FEL oscillator operating in the visible is under development at the ATF, utilizing a novel 8.8 mm period superconducting wiggler magnet. The Touschek lifetime of the 750 MeV VUV Ring at the NSLS has received much study, and is now well understood. Presently, a 4th harmonic bunch lengthening RF cavity is scheduled for installation in the VUV Ring in fall 1990. Key to the operation of the bunch lengthening cavity is the development of a feedback system to maintain the high degree of phase stability required. The 200 MeV storage ring being built for Phase I of the SXLS project will be commissioned in the summer of 1990. This ring is instrumented with clearing electrodes and diagnostics for a detailed study of ion trapping.

REPORT ON THE USE OF LOW ENERGY PHOTONS IN SOLID STATE RESEARCH

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This report represents a summary of a series of talks given by Ward Plummer (University of Pennsylvania), Eric Jensen (Brandeis University), and Jeff Bokor (A.T.&T. Bell Laboratories) on the use of low energy photons in solid state research. The talks centered around the linear and nonlinear response of the system to the incident photons. Clearly experiments that are based on the use of lasers will only benefit if the source can be pushed to higher energies or shorter wavelengths and further be made fully tunable. Experiments on nonlinear phenomena such as secon harmonic generation will benefit from a time structure similar to that currently available in laser sources, that is, with pulses of the order of a few psec width with high repetition rate. Many experiments of this type would be best suited to the output from a Free Electron Laser.

Photoemission experiments, on the other hand, are limited in the flux that can be directed onto the sample by space charge effects. Thus the natural source for this type of experiment will be an undulator based on a storage ring. One further important requirement for an experiment of this type is that the undulator can be operated in a low K mode to suppress the photon flux in the higher harmonics.

The talks presented at the Workshop represented a particular type of experiment. Other areas of research that might be explored in future discussions include light scattering, Raman spectroscopy in the Solid State and time resolved experiments related to Surface Chemistry. Experiments of the latter type where the aim is to identify well defined intermediates in surface chemical reactions are currently being carried out in high flux EELS experiments. With sufficient flux it should be possible to perform photoemission experiments on the intermediates. Further within the field of Photochemistry, either on Surfaces or in the Gas Phase, the tunability of the source will be particularly important in allowing state selective excitation.

(Ultra) High Resolution Photoemission

Angle resolved photoemission (ARPES) is currently one of the primary tools available for the study of the electronic structure of solids. It has been applied with considerable success to determine both the bulk and surface bandstructures of metals, semiconductors, and alloys. Self-energy or lifetime effects reduce the requirement for high energy resolution when studying states well removed from the Fermi level. There are, however, many examples of materials whose properties reflect the electronic structure right at the Fermi level, where the self-energy corrections should be minimal. These include the new High T_c Superconductors and the heavy fermion systems. Indeed the limited high resolution studies of these materials have already yielded valuable information. In the case of the superconductors, low temperature photoemission studies have revealed, directly, the presence of the gap (Olson, 1989). All of these studies are, however, currently limited by the energy and momentum resolution achievable with present light sources.

What energy and momentum is required in such an experiment? To date the highest energy resolution that has been achieved is approximately 20 meV, the highest momentum resolution approximately 0.05 $Å^{-1}$. These are in a study of metallic surface states by Kevan (1983). To improve and extend the experiment, one would like to achieve an energy resolution of 10 meV or less and a momentum resolution of the order of 0.01 $Å^{-1}$. Unfortunately, space charge effects place severe constraints on the number of photons that can be directed at the sample. A simple calculation leads naturally to the properties of the desired source.

If we consider incident photons of energy 10 eV, then the kinetic energy, E_k, of the electrons emitted from the Fermi level will, for a typical material, be 5.0 eV. A $k_\parallel$ momentum resolution of 0.01 $Å^{-1}$ then gives from

$$k_\parallel = 0.5123 E_k^{1/2} \sin\theta_m$$

a restriction on the included collection angle θ_m of 0.5°. Space charge effects then restrict the maximum allowed current I_m into this solid angle through

$$I_m = 38.5 E_k^{3/2} \tan^2\theta_m$$

Thus the maximum allowed current is approximately 0.03 μ amps. Allowing for a photoefficiency of the order of 10^{-2} to 10^{-3} and a monochromator transmission of the order of 1%, this translates into a photon flux in the range 10^{15} - 10^{16} photons/sec.

Nonlinear Harmonic Generation

Research into Nonlinear Phenomena began with the introduction of the laser in the early sixties. Subject areas include Second Harmonic Generation, Two Photon Photoemission, and Sum Frequency Generation. Whilst linear response in the form of photoemission examines the single or quasiparticle spectrum, nonlinear response provides a measure of the collective response of the system to an external field. Clearly, a detailed understanding of these phenomena are needed in the technologically important field of Nonlinear Optics.

The linear response of a jellium surface has been calculated (Feibelman) and shown to be correct in the pioneering demonstration of the surface photoeffect by Plummer and Levinson. The nonlinear response of the jellium system can now be calculated within both the LDA and RPA formulism. These theories can, however, only be tested at certain frequencies characteristic of lab-based lasers. The availability of a fully tunable source would allow these theories to be tested rigorously throughout the frequency spectrum. Tunability will allow a more complete examination of the excitation modes of a system such as the bulk and surface plasmons in both simple and transition metals. Recent experiments have demonstrated a negative dispersion for the surface plasmon modes on alkali metals in agreement with first principles quantum mechanical calculations. However, on silver surfaces, i.e., beyond the jellium approximation, experiments find a positive dispersion for the surface plasmons and, moreover,

a face dependence in the plasmon energies. These observations are thought to reflect the coupling of interband transitions to the dielectric response.

Another important application of non linear techniques will be in the area of interface science. Photoemission has proved invaluable in the study of the electronic structure of surfaces, but the escape depth of the electrons limits its applicability to the buried interface. Experiments which use photon-in, photon-out techniques will be more sensitive to the interface and, in particular, second harmonic generation will provide information on the electronic structure. It has further already been demonstrated that the same technique provides information on the growth mode of thin films.

Two photon photoemission has already been used to study two-dimensional surface states in metallic systems. Indeed, it has proved the source of the highest resolution information available on the binding energies and effective masses of the image states. These latter states have proved the easiest to study by two photon techniques because of their lifetimes. However, measurements of their dispersion have often been hampered by their finite lifetime. It may, therefore, be anticipated that the technique will see its widest application in the field of semiconductors.

PRIMARY PHOTOCHEMISTRY WITH A VUV-FEL

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W. A. Chupka, Chem. Dept., Yale Univ.
E. R. Grant, Chem. Dept., Purdue Univ.

Laboratory-based lasers have largely replaced other light sources for the production of radiation from the near infrared (1000 nm) to the near UV (200 nm). In particular, high peak power laser systems, e.g., Q-switched, Nd:YAG pumped lasers with tunable visible and UV light, have permitted the study of molecular excited state dynamics at unprecedented levels of detail. Such "state-to-state" studies are of central importance as they provide a clear view of the energy and angular momentum transfers important for understanding unimolecular decay processes. Below 200 nm, the poor transmittance of most optical materials limits the efficiency of VUV production by second harmonic generation. Typically, third harmonic generation schemes in atomic and molecular gases are used to produce radiation below 200 nm, however, the conversion efficiencies are quite small ($\leq 10^{-5}$). As a result, very few studies with state-selective detection have been performed in the VUV, despite the importance of this wavelength region to rarefied plasma dynamics, astrophysics, and primary atmospheric photochemistry. Indeed, many investigations involving highly excited molecules would be greatly enhanced by laser-like VUV radiation and the development of such sources using FEL technology would be of great value to chemical physics.

This report summarizes several potential applications of a high power VUV-FEL as identified by the authors. Overall, these experiments require a pulsed VUV radiation source with peak powers far exceeding what can be expected from VUV laser sources in the near future. Other criteria, including pulse width, repetition rate, and bandwidth vary among the experiments, however, properties comparable to current lasers would maximize the FEL flexibility. Clearly, the areas addressed reflect the interests of those attending the workshop and it is hoped that future meetings will address other novel applications of a VUV-FEL for photo-induced chemistry.

Proposed Areas of Research

A wide variety of new measurements in the VUV were discussed and can be summarized as follows:

- "Single Molecule" Photoionization Detector
- Dynamics of Highly Excited States
- Gas-Phase Photochemistry
- Surface Photochemistry

For the most part, the feasibility of these experiments is based on the output characteristics of the proposed FEL-MOPA device. This combination of FEL oscillator and wiggler amplifier is expected to provide ~1 mj of tunable VUV radiation at repetition rates comparable to commercial lasers (50-200 Hz) to be used at the experimental end station. The latter characteristic is important because most of the measurements proposed are true "pump-probe" experiments, in which the VUV pulse is used in conjunction with other lasers to excite and to state-selectively probe product populations.

FEL-MOPA as a Photoionization Detector

The high VUV photon intensities expected for the FEL-MOPA device make this source ideally suited as a *universal* ionization source for very dilute molecular species and products. For typical molecular photoionization cross sections of $1x10^{-17}$ cm^2, we could expect from 10% to 100% ionization within the FEL beam diameter. With efficient ion collection, this source would be nearly a *single molecule* detector. This approach is applicable to any molecular system and does not require prior knowledge of the rovibronic spectrum as does Resonant Multiphoton Ionization (REMPI) or Laser Induced Fluorescence (LIF). Furthermore, the narrow bandwidth ($\sim 10^{-4}$) of the FEL and the sharp threshold behavior of photoionization are tremendous improvements over electron impact ionization sources.

The high sensitivity of an FEL photoionization detector could be used to study the ionization potentials, dissociation energies, and heats of formation for molecular species which are highly reactive and usually difficult to produce except at very low densities. Such information is scarce for many radical species important in combustion and atmospheric reactions. For example, this high sensitivity should enable the characterization of product yield and kinetics for many radical reactions produced in flow tubes and shock tubes. Investigations of inelastic and reactive scattering in molecular beams could also gain tremendously from the sensitivity and tunability of an FEL photoionization source as important reactions with low cross sections ($\leq 10^{-2}$ Å^2) could then be studied. In combination with photoelectron spectroscopy, it should also be possible to obtain final vibronic state information on product molecules by measuring vibrationally resolved spectra. Other novel areas of application include surface chemistry and materials research which currently use electron impact ionization for detection of neutral species. The FEL photoionization detector could provide an extremely sensitive probe for molecular species thermally desorbed or photodesorbed from reactive surfaces as well as investigating neutral particle size distributions in photoablation and ion bombardment. These measurements provide the information on neutral products necessary to complete the description of Photon Stimulated Desorption/Desorption Induced by Electronic Transitions (PSD/DIET) and Secondary Ion Mass Spectroscopy (SIMS) surface probes which presently detect only ionic species.

Dynamics of highly excited states

As the excitation energy is increased to near the ionization threshold, molecules are much less likely to de-excite via direct spontaneous emission to lower electronic levels. Such highly

excited states more readily decay by internal conversion to nearby states with high level density or undergo dissociation into atomic and/or molecular fragments. At even higher energies, ionization leading to the molecular ion and free electron becomes the dominant process. The ionization efficiency of most molecules, however, is not unity for several eV above threshold indicating that neutral decay processes still occur. The most important processes involve the decay of discrete neutral levels lying above the ionization potential, referred to as *superexcited* states. Superexcited states can non-radiatively decay by dissociation into neutral fragments or by coupling to the ionization continuum via autoionization. In photoabsorbtion and photoionization spectra, these states appear as "resonances" with widths and line shapes characteristic of their lifetime and coupling with various exit channels. By experimentally characterizing the products following resonant excitation of these superexcited states (ions, photoelectrons, and photofragments), we can probe the dynamics of the scattering process.

Single-photon VUV studies have provided much of the ground work in this area, however, these experiments are often severely limited by spectral congestion as well as unfavorable geometry changes between the ground and excited states of the molecule. Photoselection followed by photoionization in laser-induced resonant multiphoton ionization (REMPI) eliminates many of these difficulties through selective excitation pathways which can lead to a single *rovibronic* level. In conjunction with tunable UV/VIS lasers, the FEL could be used for either photoselection of highly excited states in the VUV or photoionization of levels prepared by n-photon excitation. In the former role, the FEL can reach excited states via a one-photon process and thereby produce near saturated populations. As an ionization probe, the FEL will allow a much larger number of super-excited states to be accessed, especially those Rydberg levels converging to excited electronic states of the ion.

Photoselection and REMPI can also be used to investigate shape resonance phenomena which result from resonant "trapping" of an outgoing photoelectron by quasi-discrete states lying in the continuum. Such phenomena, are extremely sensitive to the molecular geometry as the resonance reflects the coupling of electronic and nuclear motions. REMPI techniques permit one to vary the nuclear coordinates by preparing different vibrational levels, but laser-only measurements usually do not have sufficient energy tunability in the ionization step to fully probe the large width characteristic of shape resonances (typically 5 eV). Using the FEL as an ionization probe, it should be possible to cover the entire width of the shape resonance region as well as reach shape resonances associated with more tightly bound valence electrons.

Gas-Phase Photochemistry

Investigations of the primary photochemistry of small molecules generally requires UV/VUV radiation with energies greater than 5 eV ($\leq$248 nm). In addition, the dissociation laser must be very intense in order to produce large yields of photofragments which can be subsequently probed by other spectroscopic techniques such as laser-induced fluorescence (LIF) or resonant multiphoton ionization (REMPI). Fixed-frequency excimer or Nd:YAG lasers producing 10-40 MW of peak power are typically used for such studies, however, only two

intense excimer lines at 193 nm (ArF) and 157 nm (F_2) lie below 200 nm. Clearly, an intense and tunable source, such as an FEL, is needed to extend these studies into the VUV.

The pulse intensities required for state-resolved photodissociation measurements can be estimated by establishing the minimum yield of photoproducts needed for LIF and/or REMPI detection with current UV-VIS probe lasers. A requisite product yield of $\geq 10^6$ per quantum state can be estimated for atomic products or simple diatomic fragments, e.g., OH, CN, NO, which have been probed by various techniques in many previous studies of polyatomic photodissociation. Larger polyatomic photofragments will be produced over a larger distribution of rovibrational levels so that many more total products must be produced by the excitation process. Furthermore, final state probes may only sample a few percent of the molecules in any one quantum state, e.g., Doppler profile measurements, further increasing the total photoproduct yield needed to $\sim 10^{10}$ per pulse. Assuming an absorption cross section of $1\text{-}10 \times 10^{-18}$ cm^2, we estimate the intensity for a viable VUV photochemistry source to be 10^{15}-10^{16} photons per pulse. At 150 nm, this corresponds to 1-10 mj of pulse energy. Throughout we assume that the VUV absorption process is linear, so that it is important to keep the peak power less than ≤ 100 MW. This corresponds to FEL pulse widths of 0.1-1 nsec. For much shorter pulses and, consequently, much higher peak powers, non-linear multiphoton absorption could take place and significantly alter the observed dynamics. As state-resolved photochemistry experiments make the greatest demands on the VUV pulse energy, it is expected that 1-10 mj per pulse is an upper limit for the chemical physics experiments proposed in this workshop.

Given these characteristics, it will be possible to investigate the photodissociation dynamics of small molecular systems important in atmospheric and combustion chemistry. These include H_2O, HCN, CO_2, N_2O, NO_2, CH_4, C_2H_2, NH_3, and CF_2Cl_2, as well many hydrocarbon radicals which have high dissociation energies (e.g., CH_3). The tunability of the FEL will allow selective excitation of Rydberg and valence states whereas previous state-resolved studies on systems, such as H_2O, were performed at fixed-frequencies determined by the laser (193 nm or 157 nm) and not by the spectroscopy of the molecule. By measuring the internal and translational energies (scalar correlations), and spatial distributions (vector correlations) of the fragments, it will be possible to determine the dynamics of the dissociation event and provide new tests for accurate potential surfaces. In addition, these measurements can provide quantitative yields of the alternative photoproducts, e.g., $O(^1D,^3P)$ or OH(X,A,B), knowledge of which is important for modeling photochemically-driven reactions.

Surface Photochemistry

Recent experiments in molecular beam surface scattering and thermal desorption have demonstrated the usefulness of laser probes (LIF and REMPI) for determining the rovibrational state populations ("temperature") of the scattered or desorbed molecules. In general, these measurements can provide information on molecule-surface dynamics at a level of detail not possible with conventional surface chemistry probes, i.e., photoemission, LEED, and mass spectrometry. As noted above, these states-selective probes can be used to derive the scalar and vector correlations in gas-phase photodissociation which provide a detailed dynamical picture of

the fragmentation process. The analogous surface process, photon stimulated desorption (PSD), involves photon absorption leading to breaking of the surface chemical bond and energy redistribution in the desorbed *neutral* molecular species. Production of neutral molecules by resonant electronic excitation has been suggested as an important desorption channel, however, very few experiments have been conducted at photon energies where electronic excitation competes with ionization (≤ 10 eV). Recent electron impact studies of CO and NO on platinum surfaces, show that neutral desorption yields have thresholds near 5 eV. Other studies of chemisorbed NO using the 193 nm excimer line have shown extremely interesting dynamical effects including non-Boltzman rotational distributions and preferred final state channels. The FEL-MOPA device could provide the high intensity and tunability necessary to perform these measurements throughout the VUV in an effort to explore the energy dependence of PSD. By measuring the rovibrational and translational energy distributions as a function of excitation energy it may be possible to determine if PSD results from direct dissociation on a repulsive molecule-surface potential or involves a secondary transition to a loosely bound surface molecule. Related measurements include photodissociative desorption in which VUV radiation photodissociates chemisorbed molecules and the "hot" photofragments desorb from the surface. It is expected that the measured photodissociation dynamics will differ significantly from the gas-phase and can be related to the initial chemisorption bond. These studies could be important for understanding laser induced deposition and ablation processes.

BIOLOGICAL APPLICATIONS OF VUV RADIATION

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Introduction

The session of biological applications of FELs focused on three types of experiments: UV damage of DNA, Raman spectroscopy, and time resolved fluorescence spectroscopy. These topics were chosen both because they require photon sources with properties similar to those provided by FELs and/or undulators and because of the interests of potential users from the local area.

Ultraviolet Radiation Damage *in vitro* and *in vivo*

The biological effects of UV on individual cells include reduced growth, the induction of mutations, and death. In humans, UV is responsible for erythema (sunburn), tanning, premature aging of the skin, and cataracts. UV also causes changes in the immune systems of man and other mammals. The biological effects of UV have been of interest because it is an excellent model system for studying DNA damage and repair, effects which are important in carcinogenesis. Insights gained from UV studies have advanced our understanding of the biological effects of ionizing radiation and chemical carcinogens. Understanding of the biological effects of UV has become critically important because of the need to make realistic forecasts of the consequences of the depletion of stratospheric ozone. The mechanism of action of UV on biological targets depends critically on the wavelength of the radiation. Most of the detrimental effects of UV for wavelengths present in the solar spectrum at the surface of the earth are associated with damage of DNA. Three regions of the UV with distinctly different biological activities have been identified.

$320 < \lambda < 400$ nm:

The major biomolecules [DNA, RNA, and proteins] absorb weakly, if at all in this spectral region, but the intensity of solar radiation reaching the surface of the earth is high. Direct damage of DNA has been reported for wavelengths up to 365 nm. However, longer wavelengths are known to be biologically active as they can kill and induce mutations in bacteria and induce melanization (tanning) of human skin. The cross section for damaging unshielded DNA is six to seven decades lower at 365 nm compared to its peak at 260 nm and three to four decades lower than at 300 nm. The region from 320 to 380 may still contribute significantly to the total UV burden from sunlight because of the correspondingly higher solar fluxes at the longer wavelengths. The ability to accurately quantify the biological effects of wavelengths greater than 320 nm is as important in predicting the effects of ozone depletion as it is at shorter wavelengths *(vide infra)* because the solar flux in this spectral region will **not** be affected by ozone depletion. A significant experimental difficulty at the present time in studying UV damage *in vivo* is that conventional monochromatic sources require long periods to produce

enough light to result in measurable damage. However, living systems actively repair UV induced lesions in their DNA. If the time or irradiation is long compared to the time for significant repair, the true cross section for lesion induction cannot be measured accurately. Very intense photon beams, as from an FEL, would make possible more accurate measurements of damage in living systems. In addition, the continuous tunability of an FEL would make possible continuous coverage of the spectrum, rather than limiting measurements to a few wavelengths, as happens when the source is a high pressure Hg arc/monochromator. Table I gives estimates of the photon beam power required for several biological experiments at 365 nm.

TABLE I

BIOLOGICAL END POINT	POWER REQUIRED AT 365 nm
killing mammalian cells in culture . e^{-1}, 1 cm area, 10 sec exposure	600 Mw
melanoma induction is fish, 4 cm area, 5 min exposure	1.6 W
minimum erythema in lightly pigmented human skin, 4 cm area, average for 6 volunteers exposure time = 10 min	400 Mw
detectable pyrimidine dimers in crop plants	????

While the estimates vary for the different experimental systems, all values are in the vicinity of total beam power of a Watt. Two types of limitations must be considered in proposals to use high power photon beams from an FEL in these experiments: power loading of the window separating the experiment, which is at atmospheric pressure, from the UHV of the FEL. Fortunately, for $\lambda > 150$ nm, high quality quartz windows are available. Presumably, the beam can be expanded and spread over a sufficient area such that the window can stand the thermal load (but detailed calculations will be required). Data on damage to the optical properties of the quartz (i.e., solarization) should be obtainable from studies with conventional lasers where equivalent flux densities can be generated over small areas. The second area of concern is thermal loading of the biological target, which is not the matter of interest. We estimate by extrapolation that the power density to produce a minimum erythemal response in a fair skinned human in one minute is one Watt/cm^2. The same response could be produced in ten minutes with a flux density of 100 Mw/cm^2, a time that should still be short enough to exclude significant repair. Human skin can clearly tolerate this power density since the solar flux at the surface of the earth on a cloudless day with the sun at the zenith is >100 Mw/cm^2. However, power densities of a W/cm^2 are probably too great to avoid thermal effects. Green plants can obviously tolerate power densities >100 Mw/cm^2, and probably much higher ones since significant power is absorbed without the generation of heat by photosynthesis.

However, while critically important in predicting the biological effects of ozone depletion, not enough is known about the cross section for damaging plant DNA and the rate at which DNA damage can be repaired to predict the power densities that will be required to observe these effects.

$280 < \lambda < 320$ nm:

The changes in insolation that will result from ozone depletion will appear almost exclusively in this spectral region. Thus, accurate knowledge of the cross section for DNA damage in various biological systems is crucial in formulating accurate predictions of the biological effects of ozone depletion. Between 320 and 300 nm, the cross section for damaging unshielded DNA increases by about two orders of magnitude. Thus, the requirements for high power densities decreases at the shorter wavelengths for some of the interesting biological targets. In the case of crop plants, however, it may be that high power densities will be required even at the shorter wavelengths. In any event, there is a need for a source that can deliver the needed fluxes with a suitably narrow spectral band width, since the steep slope of the DNA cross section versus wavelength heavily weights the shorter wavelength components of broad band excitation to shift the apparent cross section function to shorter wavelengths. Complete wavelength tunability is the other desirable property of a source for studying DNA damage in this region. Desirable properties for a source for probing the biological effects of UV as related to ozone depletion are given in Table II.

TABLE II

Wavelength Tuning Range	280 - 400 nm
Time Structure	continuous micropulses
Spectral Band Width	$\Delta \lambda/\lambda < 3 \bullet 10^{-4}$
Wavelength Switching Time	$< 10^{2}$ sec desirable $< 10^{3}$ sec acceptable
Power, time average	> 500 Mw

$\lambda < 280$ nm:

The cross section for damaging DNA reaches a maximum, but there is no reasonable likelihood that solar radiation in this spectral region will ever reach the earth. Conventional sources are generally adequate for wavelengths greater than 200 nm. There is considerable interest, principally in Japan, in studying the effects of wavelengths less than 200 nm on DNA and other biological molecules. The rationale is that the effects of these wavelengths mimic some of the properties of ionizing radiation. Experiments to produce characterizable quantities

of VUV photoproducts have been hampered by the fluxes available from the Tokyo synchrotron, and an intense, tunable source would, no doubt, be of interest to scientists who are working in this area.

Spectroscopy

Raman Spectroscopy

Raman spectroscopy uses visible, ultraviolet, and near infrared photons to provide information about the vibrational modes of molecules. Unlike other forms of electronic (visible & UV) spectroscopy, the vibrational bands are relatively narrow and hence there tends to be less spectral overlap. Thus, for example, in DNA one can see resolved transitions associated with each of the four bases, the sugar moieties, and the phosphate groups. In contrast, in UV absorption, the spectra of the four bases overlap strongly and the sugars and phosphates are spectroscopically silent. Similar information could be obtained from IR spectra. However, while water, the canonical environment for biology, absorbs strongly in the IR, it is a poor Raman scatterer.

The cross section for Raman scattering increases by orders of magnitude for wavelengths corresponding to electronic transitions. This "resonance" Raman effect greatly increases the sensitivity of the method and has been exploited for some years in studies of molecules that contain some component that absorbs strongly in the visible--heme proteins, for example. With the advent of UV lasers, the forefront of resonance Raman spectroscopy of biological materials has shifted to molecules that absorb only in the UV: nucleic acids, proteins without prosthetic groups, saccharides, and lipids. Present conventional lasers restrict the stimulating wavelength to a limited number of discrete lines, albeit an increasingly larger number. Continuous tunability from a single laser would be desirable. The power available from conventional lasers is also limiting for some experiments and at some wavelengths, although beam powers greater than a few Mw are likely to degrade many biological samples. Artifacts due to photodamaged samples can be avoided if necessary by continuous replenishment of the sample, particularly in kinetic experiments involving flow mixing. Time structure of the photon beam is useful both for separating Raman scattering from fluorescence and in kinetic experiments.

Wavelengths less than 180 nm are likely to be of limited interest because the scattering cross section of water will also be enhanced by resonance. Wavelength switching times of 10^2 s would be ideal and 10^3 s acceptable.

Spectral purity is a concern in using FELs for Raman spectroscopy. For the conventional lasers used for Raman spectroscopy, $\Delta\lambda/\lambda$ is typically $2 \bullet 10^{-5}$ (a 10 Ghz bandwidth @ 500 nm), while for proposed FELs, values of $\Delta\lambda/\lambda = 10^{-4}$ have been discussed. This may not be a fatal problem, however, since in present Raman experiments, the resolution of the spectrum is not limited by the line width of the laser, but by the spectral band pass of the detection system. Typical lines are 5 to 10 cm^{-1} in width, which at 200 nm (= 50,000 cm^{-1}) corresponds to $\Delta\lambda/\lambda$

$= 1$ or $2 \bullet 10^4$. Hence, the spectral width introduced by an FEL would be comparable to widths introduced by other subsystems in a Raman spectrometer.

Time Resolved Fluorescence

Fluorescence[1] spectroscopy using visible and UV excitation is a widely used tool in studies of biological structures. It is often more sensitive to the local environment of a fluorophore than is simple absorption spectroscopy and provides more analytical "handles": quantum yield, excitation and emission spectra, linear polarization anisotropy, the time course of the decay of both intensity and anisotropy, and greater sensitivity to temperature, pressure, solvent, and quenchers. Information can be obtained on the properties of the system both before and after absorption of a photon. The latter is particularly useful in studies of photochemical reactions, e.g., photosynthesis and UV damage.

As in Raman spectroscopy and UV damage studies, the ability to select any excitation wavelength at will is a potential advantage of FELs in fluorescence spectroscopy. Interference from the absorption of water limits the spectral region of interest to wavelengths greater than about 180 nm. Present UV laboratory-based lasers frequently lack the intensity required for more demanding experiments and beam powers greater than a few Mw may degrade biological samples. Artifacts due to photodamaged samples can be avoided, if necessary, by continuous replenishment of the sample, particularly in kinetic experiments involving flow mixing. Usually, spectral purity is not an important consideration and $\Delta\lambda/\lambda = 10^{-4}$ would be more than adequate.

The time structure of the photon beam is of great importance in the measurements of fluorescence and polarization anisotropy decay rates. Ideally, one would want an intense pulse with duration of a few ps and repetition rate of about a Mhz. Wavelength switching times of 10^2 s would be desirable and 10^3 s acceptable. The ability to scan the wavelength of the exciting photon beam continuously, while convenient, is not necessary for most work.

[1] Fluorescence denotes emission from an excited state to a ground state of the same spin multiplicity. For the overwhelming majority of molecules of interest in biological systems, these are singlet states. The term luminescence includes both fluorescence and phosphorescence. The latter denotes emission of a photon that occurs in conjunction with a change in spin multiplicity; usually an excited triplet state that radiatively decays to a singlet ground state. Phosphorescence is also used in studies of biological structures, albeit to a lesser extent than fluorescence. Time structure considerations are different for fluorescence and phosphorescence. Characteristic lifetimes for fluorescence range from a few ps to a few hundred ns, while for phosphorescence, decay times range from μs to tens of seconds.

CONCLUSIONS AND RECOMMENDATIONS

It is clear that a broad range of science can be made possible by the creation of new, or utilization of existing, intense VUV sources. This last point suggests that a proposal for the utilization of U-13 in this energy range be developed immediately, as the only competitive source in the United States (the ALS U-10 undulator line) is still some several years in the future. The establishment of such a facility could have a major impact on any future source development, by galvanizing a community of users of intense VUV sources. The experience they would gain in moving from lab-based lasers to accelerator-based sources will be invaluable to the design of the next generation of both sources and experiments, and in establishing the scientific credibility of any proposed project.

The U-13 undulator cannot, however, serve the needs of the entire community expressed during the workshop and subsequent discussions. While it has the tunability which was almost universally regarded as crucial to a useful VUV source, its time structure cannot be varied dramatically, and its peak power is far below that which would be required for many of the experimental programs discussed during the workshop.

It is therefore imperative that planning for a realistic set of sources commence immediately in consultation with the potential users. Several parameters need much clearer definition, in particular, the time structure or range of time structures a new source could provide, and the requirements for peak and average power. One other aspect of the source design which will require immediate attention is the requirement for optics, which covers issues such as spectral resolution and purity. If required, the need to introduce optics in an FEL experiment could have a severe impact on the actual peak power and bandwidth which is ultimately delivered to the experiment. The following recommendations can therefore be made:

1) Investigate the requirements for instrumentation of U-13 to provide photons in the VUV and submit a proposal for funding at the earliest possible time.

2) Establish working groups to explore new sources in more detail. In particular, define limits for the operating parameters of the experiments and work back to the source, pursuing both FEL and storage ring based technologies simultaneously. It is crucial to introduce an assessment of the required optical systems as early as possible.

3) Based on the results of the previous, hold an open workshop on VUV science, and any credible source we might develop in the near future.