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## Workshop on Scientific and Industrial Applications of Free Electron Lasers

F. C. Difilippo  
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WORKSHOP ON SCIENTIFIC AND INDUSTRIAL APPLICATIONS  
OF FREE ELECTRON LASERS

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## ACKNOWLEDGMENTS

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## ABSTRACT

A Workshop on Scientific and Industrial Applications of Free Electron Lasers was organized to address potential uses of a Free Electron Laser in the infrared wavelength region. A total of 13 speakers from national laboratories, universities, and the industry gave seminars to an average audience of 30 persons during June 12 and 13, 1989.

The areas covered were: Free Electron Laser Technology, Chemistry and Surface Science, Atomic and Molecular Physics, Condensed Matter, and Biomedical Applications, Optical Damage, and Optoelectronics.



## 1. INTRODUCTION

Over the past three years, a significant number of experiments which use the free electron laser (FEL) as a photon source have been reported. These experiments range from solid state physics, surface chemistry, optical damage studies and nonlinear optics to medical and biomedical studies. We are seeing a transition in the use of FELs from the study of FEL physics to their use as photon sources in an extraordinarily wide range of scientific disciplines.

In the next few years, the Free Electron Laser (FEL), with its unequaled combination of broad wavelength coverage, high peak and average power, ultra-short pulse length, and variable time structure, will become a major tool for the study of photon interactions with matter. This unique device has been perceived world-wide as being capable of opening up as-yet unexplored research and application areas in condensed matter physics, chemistry, material sciences, and biophysics.

In a recent DOE-sponsored workshop\* held at Lawrence Berkeley Laboratory, the more than 50 participating scientists representing the fields of chemistry, surface science, condensed matter physics, and industrial applications issued the following statement: "The Free Electron Laser shows great promise of having a major impact in many areas of science and technology—an impact similar to those of the ultrahigh vacuum system, the computer, and the conventional laser."

In the past year, the United States FEL community has become aware of the extent of the Japanese FEL effort. The Japanese have sent several delegations to the United States this year to study FEL's, and another will be in the U.S. shortly. These groups have been working in part under the sponsorship of the Optoelectronics Industry Technology Development Association (OITDA). This sponsorship demonstrates that the Japanese government and industry have identified optoelectronics as a major growth area and that the FEL is regarded as a driver technology within that area. Further, if one views Europe in terms of European Community (E.C.) '92, the European FEL program is only slightly smaller than the Japanese, with major FEL programs in Germany, France, the Netherlands, England, and Italy. Representatives of the European FEL community have met annually for several years to review results and discuss future directions.

In 1984, the Congress established a national program for the exploration of medical and bio-medical applications of FEL's, the Medical FEL Program, which

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\*A. H. Kung "Report of the Workshop on Scientific Opportunities for Infrared Free-Electron Lasers," Lawrence Berkeley Laboratory, LBL-26783, CONF-8810126, UC-400.

is administered by the Strategic Defense Initiative Organization. That program originally had a Materials Science component, but that portion of the program has been significantly reduced in scope. This program is the only major source of support for non-weapons FEL-based research in the U.S. This situation is of considerable concern to the U.S. FEL community.

Indeed there are only three FEL facilities available for civilian use in the U.S.: one at the University of California at Santa Barbara (far infrared) and two at the Vanderbilt and Duke Universities—both under construction and mainly for medical applications. Note that because of academic regulations, it is difficult for the industry to perform research involving proprietary information.

The purpose of this workshop was to explore the potential uses of an FEL in the infrared wavelength region, in the fields of Materials Science, Chemistry, and Solid State Physics, since there are strong programs in these areas in the ORNL and University of Tennessee scientific community.

## 2. WORKSHOP AGENDA

### Workshop on Scientific and Industrial Applications of Free Electron Laser

June 12-13, 1989, 8:30 a.m. - 5:00 p.m.

Conference Room - Building 6010

Oak Ridge National Laboratory

Oak Ridge, Tennessee

#### Program

#### Monday, June 12, 1989

- 8:30 - 9:00 a.m. Registration
- 9:00 - 9:15 a.m. Welcome and Opening Remarks, F. C. Mainschein, Director, Engineering Physics and Mathematics Division, R. W. Peelle, Section Head, Nuclear Data Measurements and Evaluation, ORNL

#### FEL Technology

- 9:15 - 9:45 a.m. "The ORELAFEL: A Free Electron Laser Using ORELA Facility as an Electron Source," Rafael B. Perez, ORNL and Univ. of Tennessee, and Felix C. Difilippo, ORNL
- 9:45 - 10:15 a.m. "Description of ORELA" and tour of the facility, T. A. Lewis, ORNL
- 10:15 - 10:45 a.m. Coffee Break

#### Condensed Matter

- 10:45 - 11:30 a.m. "Local Gap States in Quasi-One-Dimensional Mixed Valence Semiconductors" Steve Conradson, LANL

#### Chemistry and Surface Sciences

- 11:30 - 12:00 noon "Laser Application in Luminescence Spectroscopy," Tuan Vo-Dinh, ORNL

- 12:00 - 1:00 p.m. Lunch
- 1:00 - 1:45 p.m. "Application of Infrared Free Electron Lasers to Chemistry and Surface Sciences," Andrew Kung, LBL
- 1:45 - 2:30 p.m. "High Sensitivity Laser Spectroscopy of Adsorbed Gas," David Lambert, General Motors Research Laboratory

Atomic and Molecular Physics

- 2:30 - 3:15 p.m. "Applications of FEL in Atomic, Molecular and Optical Physics," Robert Compton and John Miller, ORNL
- 3:15 - 3:45 p.m. Coffee Break
- 3:45 - 4:30 p.m. "Photon-Negative Ion Interaction: The Possibility of FELs for Photo Detachment Experiments," David Pegg, Department of Physics, University of Tennessee, Knoxville

**Tuesday, June 13, 1989**

- 8:30 9:00 a.m. Registration

FEL Technology  
and Experimental Physics

- 9:00 - 9:45 a.m. "Practical Considerations to Set Up a FEL User's Facility" Ken Sokoloff, Sierra Laser, Sunnyvale, CA
- 9:45 - 10:30 a.m. "Applications of Broad Band FEL's Optical Cavity to Experimental Physics," Steve Benson, Duke University, Durham, NC
- 10:30 - 11:00 a.m. Coffee Break

Optics

- 11:00 - 11:45 a.m. "Application of Infrared FEL in Nonlinear Optical Spectroscopy," Shahab Etemad, Bellcore, Red Bank, NJ

11:45 - 12:45 p.m.

Lunch

12:45 - 1:30 p.m.

"Optical Damage," H. Hunter, ORNL

**Biomedical Applications**

1:30 - 2:15 p.m.

"Photobiology," Richard Straight, Director, Laser Institute, University of Utah and VA Medical Center, Salt Lake City, UT

2:15 - 4:00 p.m.

Round Table

**List of Abbreviations:**

ORNL:

Oak Ridge National Laboratory, Oak Ridge, TN

LANL:

Los Alamos National Laboratory, Los Alamos, NM

LBL:

Lawrence Berkeley Laboratory, Berkeley, CA

ORELA:

Oak Ridge Electron Linear Accelerator,  
Oak Ridge, TN



### 3. SUMMARIES OF PRESENTATIONS



# THE ORELAFEL: A FREE ELECTRON LASER USING THE ORELA FACILITY AS AN ELECTRON SOURCE

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## 1. INTRODUCTION

The interest on free electron laser technology and applications at ORNL dates from a few years back when Dr. Alex Zucker, Laboratory Associate Director, suggested the use of this technology to enhance many areas of research at ORNL.

During the past year, Dr. B. R. Appleton, Laboratory Associate Director for Physical Sciences, and Dr. M. Rosenthal, Laboratory Deputy Director, have provided funds to initiate a study of the potential use of the ORELA Linac as a source of electrons for a free electron laser.

This study is presently carried out by a group of ORNL employees from the Engineering Physics and Mathematics Division, and the Fusion Energy Division, in cooperation with the University of Tennessee, Department of Nuclear Engineering.

## 2. THE ORELA FACILITY

The Oak Ridge Electron Linear Accelerator (ORELA) is an experimental facility dedicated to neutron spectroscopy by the "time-of-flight" (TOF) technique.

The ORELA linac impinges 50-80 KJ bursts of electrons of average energy about 140 MeV onto a water-cooled tantalum target. Neutrons are "boiled off" from the heavy metal target by the brehmsstrahlung radiation which arises from electron deceleration within the target. With a number of experimental stations and data acquisition systems available, several TOF experiments can be performed simultaneously.

The ORELA Linac has two modes of operation:

- a. Short Pulse Operation: Electron pulses between 2 and 24 ns at rep. rates between 900 and 1000 Hz. The short pulse mode is used for neutron spectroscopy in the keV and MeV spectral region.
- b. Long Pulse Operation: Electron pulses up to 1  $\mu$ s at rep. rates up to 100 Hz. The long pulse mode is used for neutron spectroscopy up to a few electron-volts.

### 3. TECHNICAL ISSUES AND CHALLENGES INVOLVED IN THE USE OF THE ORELA LINAC AS A PHOTON SOURCE

The electron beam from a RF-Linac serving as a driver for a Free Electron Laser must verify three fundamental conditions: (1) high peak current per micropulse, (2) low beam emittance and (3) low electron beam energy spread. In addition, long macropulses (10  $\mu$ s or more) are required. Besides this set of stringent beam quality requirements, the physical plant housing the FEL must satisfy the shielding and health physics requirements imposed by DOE regulations. Moreover, the ORELA operation as a powerful source of pulsed neutrons for low-energy nuclear physics work has to be kept or even enhanced.

The analysis of the present ORELA configuration and make-up yields the following set of advantage and disadvantages in meeting the above challenging technical issues:

#### (a) Advantages

- Availability of the physical plant
- Shielding and electron beam dump
- Accelerator cavities and pumping systems
- Twenty years of experience in the operation of L-band rf-linacs
- High energy (140 MeV) electron beam

#### (b) Disadvantages

- The present Pierce-type electron gun does not meet the requirements for FEL operation.
- The ORELA modulators must be modified to produce long pulses (10  $\mu$ s) with flat tops and minimum time jitter

### 4. MEETING THE CHALLENGES

Several options have been discussed in detail with accelerator specialists at the Los Alamos National Laboratory and Sierra Laser Systems (Sunnyvale, CA).

The technology to produce the high quality electron beams required for FEL operation is by now well established after the work of Madey and coworkers at Stanford and by the FEL Laboratory group at Los Alamos National Laboratory. This technology is based on the use of high-gradient acceleration RF-guns and photocathode injectors, which are presently commercially available.

Two options appear as reasonable solutions for FEL operation at the ORELA Facility:

- a. Keep the present Pierce-type electron gun for neutron production. For FEL operation, use a LaB<sub>6</sub>-cathode RF-gun placed at a 90-degree angle to the accelerator sections. In this arrangement, the electron bunches are fired into

the accelerator through an  $\alpha$  magnet which is turned off for high-energy neutron work.

- b. Install a simplified version of the Los Alamos photocathode injector for both neutron production and FEL operation. Since a FEL for research purposes does not have to meet the high power requirements necessary for SDI work, the high quantum efficiency of semi-conductor photocathode in the LANL injector, could be replaced by less efficient but more reliable metal photocathodes, capable of working under less stringent vacuum requirements.

Option (b) offers the possibility of enhancing neutron production. However, it must be kept in mind that due to the long electron macrobunches ( $10 \mu\text{s}$  or longer) needed for FEL operation, the simultaneous production of neutron and photon beams is only viable during the long-pulse operation of the ORELA Linac.

## 5. THE ORELAFEL FACILITY: A UNIQUE SOURCE OF NEUTRON, PHOTON, AND POSITRON BEAMS

Recently L. D. Hulet, T. A. Lewis, and coworkers have retrofitted the ORELA linac with a facility to convert forward scattered gamma bremsstrahlung to positrons. With the addition of a coherent light source, the ORELA Facility would become a unique world's facility for condensed matter research with neutrons, positrons, and photons. By surrounding the ORELA neutron beam with a cryogenic system, one can generate pulsed beams of cold neutrons in the meV energy range which is also covered by infrared photons and slow positrons. A variety of novel "two-color" experiments could then be arranged, whereby the FEL light will act as the pumping device in various modes of operation.

- (a) Intense pulses of coherent light are known to produce periodic structures and Raleigh-type surface waves which modify the surface of thermoelastic materials. These effects could then be studied with slow positrons methodologies.
- (b) FEL light can apply external stresses which could in principle induce changes in crystalline structures to perform transient neutron scattering research.
- (c) In combination with conventional lasers, or probes, one could study the nonlinear susceptibility of conducting polymers and inorganic crystals for the implementation of optical switches in fiber communications and, in general, for a variety of optoelectronic devices.

## 6. CONCLUSIONS

The use of the ORELA linac as a source of electrons for FEL operation hinges upon substantial changes:

- The present Pierce gun must be replaced.

- The pulse-forming network of the modulators must be modified for longer pulses with "flat" tops.
- RF stability in both amplitude and phase must be provided.

RF electron guns and photocathode injectors are presently available with the necessary requirements in emittance and electron energy spread to lase in both the IR and visible regions, at the 140-MeV electron beam energy at ORELA.

Careful and detailed studies have to be performed, to minimize the various technological risks involved in the use of the ORELA linac as a FEL driver, while keeping the role as a source of pulsed neutrons for neutron spectroscopy work. By achieving a reasonable solution to the various problems faced in the implementation of the proposed facility, the ORELAFEL would indeed be a unique users facility where a variety of light, neutron, and positron experiments could be performed simultaneously and in an interacting manner.

## Application of Infrared Free-electron Lasers to Chemistry and Surface Sciences

Andrew Kung  
Lawrence Berkeley Laboratory

The free-electron laser (FEL) potentially could have a major impact in the fields of chemistry and surface physics and surface chemistry because of its many unique capabilities. The FEL has high average power and peak power, extremely broad tunability, very high repetition rate, and picosecond pulse structure. It is particularly attractive as a research and industrial tool in the infrared-far infrared region (longer than 4 microns) where conventional lasers with the above combination of performance capabilities are simply not available. Infrared FEL technology has reached a mature stage and broad scientific applications are imminent. The following is a partial summary of discussions presented at the Workshop on Scientific Opportunities of the IRFEL held in Berkeley on October 31 - November 1, 1988. It provides some examples of how the IRFEL can be used in molecular chemistry and the surface sciences.

### Multiphoton Dissociation (MPD)

Since most chemistry are initiated by excitation in the ground electronic state of a molecule, it is important to be able to selectively introduce large amounts of energy into a molecule to excite its vibrations to the point where dissociation can occur in order to obtain a microscopic understanding of the unimolecular decay process. This can be done by thermal heating, which does not provide microscopic details of the chemical process, or by selective excitation using a laser. The tunable CO<sub>2</sub> laser has been very successful in demonstrating the usefulness of the technique. However, many important molecules, most notably the aromatic hydrocarbons, do not absorb at CO<sub>2</sub> laser wavelengths. A few other lasers can do the job only for a handful of molecules. The IRFEL can be broadly tuned and could open this powerful technique to practically all molecules of interest.

### Multiphoton Excitation (MPE)

In close connection to MPD is multiphoton excitation where the energy in the molecule instead of inducing decomposition would simply be redistributed inside the molecule and eventually dissipate via radiative decay or collision with another molecule. The mechanism and rate of intra-molecular and inter-molecular energy transfer are subjects of intense studies. Much experimental data are urgently needed to test and compare with theory. Many of

the relaxation rates are projected in the picosecond and subpicosecond regime. Here again the IRFEL is uniquely suitable for these studies.

### **Mode-selective Chemistry**

It is most desirable to be able to control chemistry rather than letting Nature take its course in determining how a molecule reacts, to manipulate the molecules such that particular reactions work well. As a starting point, one would want to drive selected vibrational resonances to saturation with powerful lasers in the infrared. A tunable IRFEL should permit extensive investigations in this area.

### **Spectroscopy of Radicals and Reactive Intermediates**

Radicals and reactive intermediates play an important role in most chemical reactions. It is essential to understand the properties and evolution of these species during the course of a reaction. Time-resolved spectroscopy is one of the most sensitive techniques available for probing these species. For the technique to be successfully applied to most reactions, a large database needs to be developed on the spectroscopy and structure of the radicals and intermediates of interest. The IRFEL is most suitable for these investigations because, firstly, it is powerful so that it can be used to produce these species by IRMPD, and secondly, it is broadly tunable so that it can access all vibrations. An ability to employ a secondly FEL will accelerate this study.

### **Isotope Separation**

IRMPD has been shown to be isotopically selective. Efforts to-date to produce rare isotopes using IRMPD for scientific, medical, and industrial applications have necessarily involved elegant schemes to synthesize molecules that absorb CO<sub>2</sub> laser photons. Such efforts have not been very successful. The synthetic schemes are complex and do not produce molecules with good stability and in large quantities. The IRFEL should allow the use of simple molecules, i.e., molecules that are commercially available or are easy to synthesize for this purpose.

### **Surface Vibration Spectroscopy**

Study of surface states and vibrations of adsorbed molecules on a monolayer or sub-monolayer coverage is intrinsically difficult in view of the minute amount of species present. An IRFEL with high peak power and picosecond pulsewidth can selectively excite these vibrational modes to saturation, thus achieving the highest probability of detecting these modes. Sensitivity in

conventional absorption spectroscopy or recently developed schemes such as surface sum-frequency up-conversion could be substantially enhanced by the IRFEL. A combination of frequency scan and polarization effects will give structural and alignment information of the bonding between molecule and surface.

### Surface Dynamics

Dynamical information such as time dependence of redistribution of surface molecules, diffusion on surfaces, desorption, energy transfer pathway and rate, and effects of internal excitation on surface reaction rates are essential to the understanding of the interaction of molecules on surfaces. Pump-and-probe techniques involving the IRFEL for selective excitation or detection in the picosecond timescale could be used for these studies.

It is foreseeable that when the IRFEL becomes available, it will stimulate many new applications and new approaches in chemistry and surface studies. The above examples are just the tip of the iceberg. An IRFEL that meets or exceeds the following performance characteristics will have the most immediate impact on the cases discussed above:

tuning range:	4-50 microns
average power:	> 1 W
micropulse duration:	~ 1 psec
micropulse energy:	100 microjoules
frequency bandwidth and stability:	~0.1 %
spatial quality	single transverse mode

## High Sensitivity Diode Laser Spectroscopy of Adsorbed Gas

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### ABSTRACT

Spectroscopy techniques used to study adsorbate vibrations are discussed. Two techniques that use tunable diode lasers, electroreflectance vibrational spectroscopy (EVS) and polarization-modulated IR reflection absorption spectroscopy (PS), are discussed in detail. Experience with these and other techniques show that the present sensitivity limit is not set by source intensity. Other sources of irreproducibility are more important. However, a tunable high-intensity infrared source could be used for exploratory surface studies that would otherwise be impossible. An outside user facility would be ideal for such studies.

The tools of surface science are an important part of modern technology. Studies of adsorbed molecules are important precursors to advances in heterogeneous catalysis, microelectronics, and electrochemistry. Vibrational spectroscopy is a source of information about molecular bonding and the adsorbate's local environment. For some applications it is important to obtain this information *in situ*. Other studies are best done in UHV where a full range of surface analysis techniques can be used.

Many techniques have been developed to obtain vibrational spectra of adsorbates.<sup>1</sup> The most widely used technique is electron energy loss spectroscopy (EELS) which requires UHV. A variety of optical techniques, which can be used *in situ*, have also been developed. The optical techniques are grouped into four categories in Table I. Techniques that use incoherent light are the first category. Raman spectroscopy is the second. The use of laser sources for reflectance is the third. Non-linear optical effects are the fourth. Each technique has its own advantages and disadvantages. Only a few investigators have used more than one technique.

In considering how a free-electron laser could advance surface vibrational spectroscopy I discuss what can be done now. I will discuss laser reflectance spectroscopy as an example. A more likely use for a free electron laser is sum frequency generation<sup>2</sup> since the limit to laser reflection spectroscopy is not set by the laser. However, this particular example is suggestive of the kind of new science that can be expected from a new optical source like the proposed free electron laser. A better laser makes possible experiments that give qualitatively new information.

As outlined in Table II, three different types of lasers have been used to study adsorbates with infrared reflection spectroscopy: gas discharge lasers, diode lasers, and lasers that use difference frequency generation. My own experience has been with the use of diode lasers.<sup>3</sup> I have used<sup>4</sup> two different spectroscopy techniques: electroreflectance vibrational spectroscopy (EVS) and polarization spectroscopy (PS). The use of EVS and PS to study CO on Ni(100) is discussed as an example.<sup>5</sup>

The CO on Ni(100) experiment was intended to measure the correspondence between local electric field and CO vibrational frequency. The measurement in UHV was compared with theory. The

measurement was also used to interpret an analogous effect observed for adsorbates on electrodes in electrochemical cells in terms of models of the double layer between electrode and electrolyte.

In EVS, an electrostatic field is used to vary the vibrational frequency of adsorbed molecules. The variation of molecular vibrational frequency with applied  $E$  field, the Stark effect, is proportional to  $E$  for an adsorbed molecule oriented by the surface. In contrast, for most gas phase molecules the Stark effect is proportional to  $E^2$ , a consequence of rotational symmetry. Even for an adsorbed molecule the effect is quite small: of order  $10^{-6} \text{ cm}^{-1}/(\text{V}/\text{cm})$ . Despite the smallness of the Stark effect, it can be used to obtain reflection spectra of adsorbates with extremely high sensitivity. In comparison with other techniques EVS is highly sensitive because it has an extremely small background. The sensitivity of most carefully designed vibrationally spectroscopy experiments is limited by the background, not by the available light. As shown in Fig. 1, in EVS an oscillatory  $E$  field is applied to the sample and the resulting modulation of reflectivity is detected. The spectrum obtained with EVS, as the laser is tuned through an isolated molecular resonance, is proportional to the derivative of the infrared reflectivity spectrum.

In PS, one obtains the infrared reflectivity spectrum. Reflectivity difference between two polarizations of incident light is measured. Light with optical  $E$  parallel to the surface ( $s$ -polarized) does not interact with adsorbed molecules to good approximation. With the proper angle of incidence, about  $5^\circ$  from grazing incidence, light with optical  $E$  in the orthogonal direction ( $p$ -polarized) interacts much more strongly with adsorbed molecules. As shown in Fig. 2, a combination of fixed polarizers before and after the sample, together with a photoelastic modulator, is used to measure  $R_s - R_p$ , the difference in reflectivity between  $s$ - and  $p$ -polarized light. If there were no background  $R_s - R_p$  would be measured. In practice, there is a background signal that varies as the laser is tuned. The background signal is extremely sensitive to the angle of incidence, the polarization direction of light from the laser, and (unless a double demodulation scheme is used) the temperature of the sample. It is found that passing the light through a small aperture increases the reproducibility of the signal, even though the signal itself is reduced, presumably because of an even larger reduction in the background signal.

A tunable diode laser was used as optical source for both EVS and PS. The laser was fabricated<sup>3</sup> using molecular beam epitaxy in our laboratory. Similar lasers have recently become commercially available. Such lasers can be tuned  $700 \text{ cm}^{-1}$  by varying heat sink temperature and diode current. The laser was operated single mode. A wavemeter was used to observe lasing frequency.<sup>6</sup> The laser tuned continuously for  $\sim 1 \text{ cm}^{-1}$  segments separated by  $\sim 2 \text{ cm}^{-1}$  gaps.

The spectra obtained with EVS and PS of a saturation coverage of CO on the Ni(100) surface, about 0.5 monolayer, are shown in Fig. 3 and Fig. 4 respectively. The EVS and PS spectra were each obtained on two different days to check reproducibility. The spectra can be analyzed to determine the Stark tuning rate in terms of the externally applied  $E$  field,  $(5.3 \pm 0.3) \times 10^{-7} \text{ cm}^{-1}/(\text{V}/\text{cm})$ . In comparison, theory predicts  $(4.7 \pm 1.1) \times 10^{-7} \text{ cm}^{-1}/(\text{V}/\text{cm})$ . The IR cross section observed in the PS spectrum is in good agreement with a previous EELS measurement. The use of a low divergence laser beam was important for this measurement. From the IR cross section the relationship between local and externally applied  $E$  field was determined. The Stark tuning rate in terms of the local  $E$  field was  $(1.4 \pm 0.3) \times 10^{-6} \text{ cm}^{-1}/(\text{V}/\text{cm})$ . Knowing the Stark tuning rate for CO on Ni, the Stark tuning rate for CO on Au could be inferred and used to check the local  $E$  field predicted by models of the double layer. Previous experiments had shown a linear correlation between electrode potential and the C-O stretch vibrational frequency for terminally bonded CO adsorbed at the metal electrolyte interface. For a Au electrode, the observed<sup>7</sup> rate is  $50 \text{ cm}^{-1}/\text{V}$ . Models of the

double layer give a relation between change in applied potential and change in local  $E$  field acting on the CO. Two models were considered: one due to Bockris, Devanathan, and Müller<sup>8</sup> that might be expected to describe a low coverage of CO; the other a simple model of a monolayer of CO on the electrode. The Stark tuning rates predicted by both models are consistent with the measurement.

In summary, I expect a new light source like the proposed free electron laser to make possible qualitatively new experiments in surface chemistry and physics. One should look for experiments made possible by short pulses and high brightness. Such experiments are likely to involve interesting new physics and chemistry.

<sup>1</sup>J. T. Yates, Jr., and T. E. Madey, *Vibrational Spectroscopy of Molecules on Surfaces* (Plenum, New York, 1987).

<sup>2</sup>X. D. Zhu, H. Suhr, and Y. R. Shen, *Phys. Rev. B* **35**, 3047 (1987).

<sup>3</sup>D. L. Partin, *Appl. Phys. Lett.* **43**, 996 (1983).

<sup>4</sup>D. K. Lambert, *Appl. Opt.* **27**, 3744 (1988).

<sup>5</sup>D. K. Lambert, *J. Chem. Phys.* **89**, 3847 (1988).

<sup>6</sup>W. J. Evans and D. K. Lambert, *Appl. Opt.* **25**, 2867 (1986).

<sup>7</sup>M. A. Tadayoni and M. J. Weaver, *Langmuir* **2**, 179 (1986).

<sup>8</sup>J. O'M. Bockris, M. A. V. Devanathan, and K. Müller, *Proc. R. Soc. London Ser. A* **274**, 55 (1962).

Table I. Summary of optical vibrational spectroscopy techniques for adsorbates.

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A. Incoherent Spectroscopy
• Subtraction of spectra
• Wavelength modulation
• Polarization modulation
• Detection of sample heating
• Emissivity
B. Raman Spectroscopy
• Surface enhanced (on noble metals)
• Unenhanced
C. Laser reflectance spectroscopy
• Surface wave
• E field modulation
• Polarization difference
D. Non-linear effects
• Coherent anti-Raman scattering
• Sum frequency generation

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Table II. Tunable IR lasers used for vibrational spectroscopy of adsorbates.

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1. Gas discharge lasers (Cornell, IBM)
• Only discrete lines available
CO <sub>2</sub> laser: ~ 100 lines spaced 2 cm <sup>-1</sup>
CW: power > 10 W.
Pulsed: length > 10 ns.
2. Diode lasers (GMR, NRL)
• Commercially developing technology
• Available in 3-30 μm range
• Single laser tunes ~ 700 cm <sup>-1</sup> max
• Primarily for CW operation
Power ~ 3 mW
tunes 1 cm <sup>-1</sup> , hops 2 cm <sup>-1</sup>
Shot noise limited ( $\Delta I/I \sim 10^{-8} \sqrt{\text{Hz}}$ )
3. Difference frequency generation (IBM, Exxon)
• 1.4-22 μm tuning range
• Pulsed operation (ns)
• ~ 1 cm <sup>-1</sup> linewidth
• MW of power available

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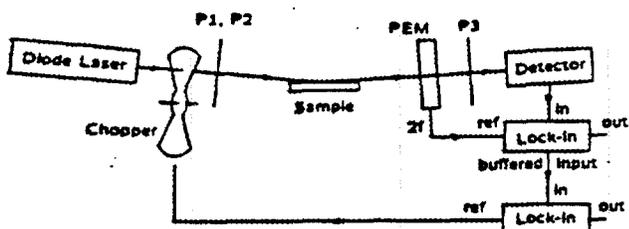


Fig. 1. Schematic of the system used for PS.

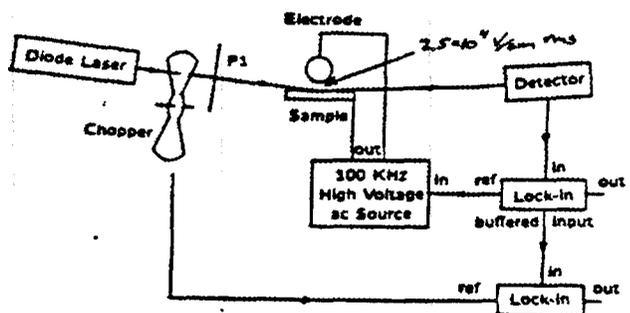


Fig. 2. Schematic of the system used for EVS.

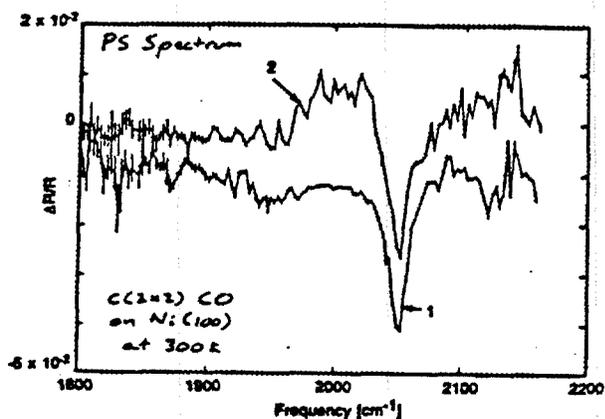


Fig. 3. Spectra obtained with PS of  $c(2 \times 2)$  CO on Ni(100) at 300 K on days 1 and 2.

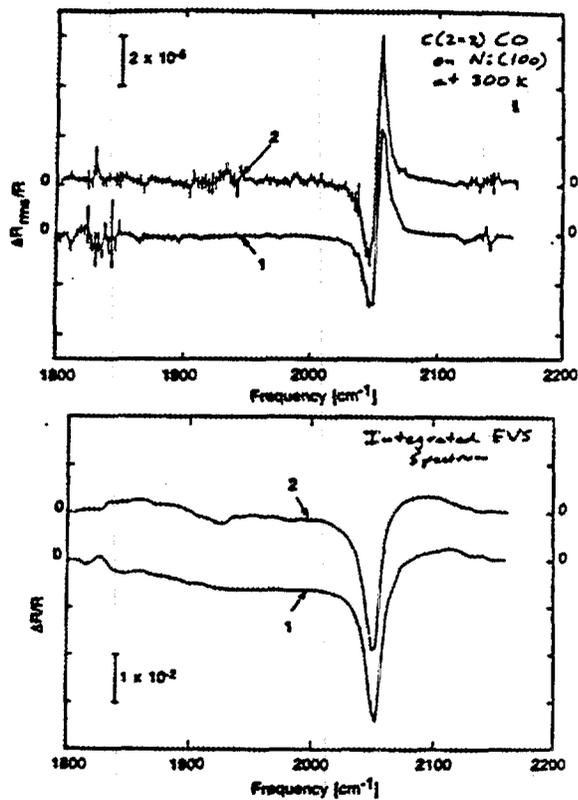


Fig. 4. Spectra obtained with EVS of  $c(2 \times 2)$  CO on Ni(100) at 300 K on days 1 and 2.

# APPLICATIONS OF FREE ELECTRON LASERS IN ATOMIC, MOLECULAR, AND OPTICAL PHYSICS

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## I. Introduction

When one considers the relative merits of a free electron laser (FEL) in the study of atomic, molecular, and optical (AMO) physics it is necessary to distinguish the FEL from the wide selection of presently available (and less expensive) tunable dye lasers. In many instances, the FEL as it exists today offers some advantages over conventional lasers (e.g. higher power, wider tunability). Since the FEL is a relatively new device, we can expect even greater power and frequency range capabilities in the future. The laser, on the other hand, offers the advantage of easily producing multiple color beams, higher power at certain frequencies, and more selectable pulse length. Many of the important problems today involve what are termed "pump-probe" experiments in which one laser is used to excite an atom or molecule (or surface) to a given excited state, and a second laser is used to further excite or ionize the excited species. The second laser then probes the excited state, which may have relaxed as a result of dynamic coupling within the excited species. The second laser may also be used to probe changes in the excited state due to external electromagnetic field mixing or collisions. Such two-color laser experiments have spawned a new era in AMO physics: state-to-state chemistry. The FEL offers many advantages in these pump-probe experiments. Thus it is our view that conventional lasers and FELs complement each other, and there are unique advantages to combining the two light sources. We mention a few such applications below.

## II. Atomic Studies

Currently there is much interest in multiphoton ionization and harmonic generation in atomic and molecular gases. Our group has been actively involved in this field using visible dye lasers. The application of high-power tunable long wavelength lasers to MPI and harmonic generation in alkali atoms would represent a new approach to understanding atoms in high optical fields. The use of dense alkali vapors may also allow for efficient up conversion of the FEL light. Tuning the FEL would examine the possible effects of atomic structure on the nonlinear interaction of light with simple atoms.

Other fundamental studies could be performed using one or more dye lasers to excite an atom to an excited state, and the FEL could be used to ionize the excited atom over a broad energy range in the continuum. Minima in the photoionization continua are theoretically expected but have not yet been observed from excited states. The exact position of the minima are difficult to calculate due to the sensitivity of the minima to the accuracy of the wave functions for the initial and final state. The FEL would allow for a wide frequency range in order to find the minima or multiple minima.

Another area of unique application of the FEL is in studies of photon interactions with negative ions. Almost all atoms in the periodic chart have a positive electron affinity and can form a stable negative ion. Although there is only one atomic negative ion (carbon) known to have a bound excited state, others are expected. On the other hand, all negative ions including  $H^-$  have excited unbound states in the form of shape and electronically excited Feshbach resonances. The FEL could be used to study the photodetachment threshold for one or more photons while structure in the photodetachment continuum

provides information as to the positions of these resonances. The long wavelength afforded by the FEL would allow for measurements of photodetachment thresholds (and therefore accurate electron affinities) for many atoms in the periodic chart. An important element in these experiments is the source of negative ions. We have developed a universal source of *pulsed* negative ions of most elements using laser ablation of a metal surface. This pulsed ion source is ideal for use with the pulsed FEL source.

We are presently collaborating with Dr. H. P. Saha (Central Florida University) on the theoretical calculations of photodetachment cross sections and negative ion resonances. In addition, we have strong and established collaborations with Dr. P. Lambropoulos (USC) and Dr. V. McCoy (Cal. Tech.) on theoretical descriptions of multiphoton ionization of neutral atoms and molecules. The use of a FEL in all of these collaborations would be warmly welcomed.

### III. Molecular Studies

A versatile, widely tunable, high power source of coherent infrared light has numerous potential applications in the spectroscopy, photophysics, and dynamics of molecular systems. This is because the vibrational frequencies of all molecules fall in the range of 2.5-25  $\mu$ —the so-called "fingerprint region." A particular molecule can thus be uniquely identified by its IR spectrum and can be quantitatively characterized in a mixture. Isotopic characterization is also readily accomplished as vibrational isotope effects of molecules are much larger than electronic isotope effects for atoms. In physical chemistry and chemical physics, vibrational analysis leads to structural information on molecules. More importantly, when energy is deposited in molecules via photoexcitation, collision, or chemical reaction, a redistribution of this energy occurs very rapidly throughout the electronic, vibrational, rotational, and translational degrees of freedom of the molecule. A quantitative mapping of this energy distribution is central to the new and exciting field of state-to-state chemistry. Selective energy deposition into vibrational motion or subsequent detection (as a function of time) of vibrational energy would be facilitated by a light source such as the FEL.

The chemical physics section at ORNL has performed, can perform, or would like to perform many such state-to-state experiments. Of particular interest is the unimolecular decay of molecules following single-quantum-state excitation by a narrow-band laser. The energy content and distribution is then probed at later times. These pump-probe experiments have traditionally been performed with two visible or ultraviolet lasers, but many such studies could involve infrared photons from a FEL as either the pump or probe. Several examples of these are described below.

#### 1. UV-VUV pump-FEL probe:

When a molecule such as  $\text{CH}_3\text{I}$  is photodissociated, say with a 266 nm laser, the molecule fragments into a  $\text{CH}_3$  radical and I atom. The molecular fragment could then be probed with a FEL pulse to give a vibration-rotation absorption spectrum which would analyze the energy content and distribution in the fragment. If this could be done as a function of time, then details of the photofragmentation dynamics would emerge.

#### 2. FEL pump-UV-VUV probe:

Van der Waals molecules, such as  $(\text{NO})_2$  molecules, have many low frequency or "floppy" vibrational modes. Following excitation of more strongly bound modes, the energy may migrate to the weaker bond leading to dissociation. This process is called vibrational predissociation. The excitation would thus be performed with

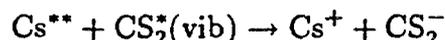
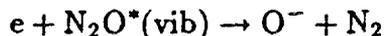
the FEL, and the probe done by UV-visible laser-induced fluorescence or multiphoton ionization. Time delaying the two lasers may provide information on the dynamical coupling between the internal modes of the molecule.

3. Combined FEL + vis/UV/VUV probe:

Infrared absorption, as mentioned in example (1.) above, is not a very sensitive technique. However, two-color fluorescence excitation or multiphoton ionization has many advantages. Here, the FEL would provide selective excitation of a molecule or a vibrational state within a molecule. Simultaneously a visible/UV/VUV pulse from a second laser would excite fluorescence or ionization, both of which allow quite sensitive detection. This combined FEL + vis/UV/VUV probe could be used in many types of experiments.

4. Isotope separation or analysis:

If the FEL is used to selectively excite the vibration of a particular isotope, then another laser can be used to ionize or otherwise detect only that isotope. This was the basis for the molecular isotope separation scheme using  $\text{UF}_6$ , for instance. Many other examples could be envisioned. Vibrationally excited molecules can also present exceptionally large cross sections for collisions with other atoms and molecules. In some cases the cross section for ground state molecules may be zero (endothermic or otherwise inhibited) whereas the same molecule with one quantum of vibration may be very large. Our group has studied many such reactions over the years using nonselective (e.g. heating) sources. A FEL would allow one to excite a specific vibrational state of a molecule and study its ensuing chemistry. A number of examples are given below:



Probing the final products with a laser or FEL is another example of state-to-state chemistry. The high power and repetition rate of the FEL combined with its wide tunability would make it an attractive source for such experiments.

5. Studies of molecular negative ions:

A FEL operating in the IR or VUV could make unique contributions to the study of molecular negative ions. As mentioned for the case of atoms, many molecules have electron affinities which are below  $\sim 0.5$  eV. This is particularly true of large organic molecules but can be generally stated about all molecules. Furthermore many molecular anions have bound excited states which could be accessed by multiple quanta absorption from a free electron laser source. The broad tunability of the FEL and its pulsed nature could be utilized with presently available pulsed nozzle jets which are capable of producing pulsed sources of high intensity ultra-cold negative molecular anions.

The IR output from a FEL could also be used to study vibrational autoionization from excited anions. For example, some years ago we showed that the  $\text{CO}_2^-$  anion existed in a metastable excited state and is readily produced by a variety of methods. The lowest state of  $\text{CO}_2^-$  has a lifetime of  $\sim 90$   $\mu\text{sec}$ . Vibrational excitation of the bent  $\text{CO}_2^-$  anion is expected to reduce the lifetime to  $\sim 10^{-14}$  sec. Thus a study of the photodetachment cross section versus photon energy would give information as to the vibrational frequencies of  $\text{CO}_2^-$  and provide the first clear information on the dynamics of vibrational autoionization of a simple anion. There are many other examples which could be cited.

In 1977 one of us discovered a class of metal hexafluoride molecules which have electron affinities well above 5 eV. Since the highest known atomic electron (EA) affinity or molecular electron affinity at that time was less than 4 eV (e.g. halogens), these  $\text{MF}_6$  species were termed "super halides." A number of experimental and theoretical studies show that  $\text{EA}(\text{PtF}_6) \sim 9 \text{ eV}$  and  $\text{EA}(\text{AuF}_6) \sim 10 \text{ eV}$ . There is even evidence that multiply charged anions of these hexafluorides might be *bound*. The VUV output from a FEL could be used to perform photodetachment studies of these anions. The experiment would involve measurement of the photodetachment threshold as well as photoelectron spectrum of  $\text{MF}_6^-$  at higher photon energies. It is possible to make very intense beams of such anions from surface ionization (e.g.  $\text{UF}_6^-$ ) and other methods so that such experiments would be possible even if the photodetachment cross sections are low. This would be especially so with an intense pulse FEL. We should also emphasize that most of these anions are expected to have bound excited states. Thus resonantly enhanced multiphoton detachment of such anions would be possible and would yield the first information on electronically excited states of these "super-halide" molecules.

## PRACTICAL CONSIDERATIONS IN DEVELOPING A FEL USERS' FACILITY

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Sierra Laser Systems, Inc.

There are three major considerations which affect the development of a FEL users' facility. It is first necessary to recognize that machine users are guided by a different philosophy than machine builders. A machine users' facility places primary emphasis on output of photons whereas a machine builders' facility is primarily concerned with pushing the edge of the technological envelope of FEL device operation and physics. This leads to the second important consideration; a machine users' facility should select a FEL with demonstrated reliability of the critical subsystems of Modulator, Electron Gun and Wiggler. Machine users should also require automated control of the device. Also, for a device as expensive and evolving as a FEL, the machine selected should be sufficiently modular to easily and inexpensively accept future improvements in FEL technology. Finally, a FEL facility must give significant weight to having appropriate laboratory space and laboratory management so researchers can easily utilize the light provided by such a rare device. The tradition at ORELA of operating a successful users' facility should increase the likelihood of a successful FEL users' program at ORNL.

PHOTON-NEGATIVE ION INTERACTIONS: THE POSSIBILITY OF FREE-ELECTRON  
LASER PHOTODETACHMENT EXPERIMENTS

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The formation of a negative atomic ion involves a delicate balance between attractive forces supplied by the nucleus and interelectronic repulsive forces. Shielding of the nucleus by the atomic electrons and correlations between the motions and spins of the electrons both play important roles in determining whether a particular negative ion will exist. The net force binding the attached electron arises from polarization and exchange effects. This relatively weak and short-ranged force results in negative ions being fragile and easily destroyed. Perhaps surprisingly, over 80% of the naturally occurring elements are able, under appropriate environmental conditions, to attach an additional electron to form a stable negative ion. Other elements are able to form long-lived metastable ions. With the exception of the halogens, the binding energy of the least-tightly bound electron in negative ions is  $<1$  eV and for many fragile ions, it is only a few tenths of an electron volt. This implies that photodetachment thresholds most frequently lie in the infrared region of the electromagnetic spectrum. The free-electron laser (FEL) could prove to be an excellent source of radiation for either single-photon or multi-photon detachment studies. The energies, tunability, fluxes, and polarizations of FEL photons appear to be well suited for crossed or merged beams experiments.

The technique of energy- and angle-resolved photoelectron detachment spectroscopy is currently being used at ORNL to determine the structure of

negative ions and to investigate the interaction between negative ions and radiation. The measurements are performed on a crossed beams apparatus. The source of the photon beam is a flashlamp-pumped dye laser operating in the visible region of the spectrum and the source of the ions is a fast moving beam produced by a small accelerator. The method involves measuring photoelectron energies, yields, and angular distributions.

The technique of determining the structure of negative ions will be illustrated using  $\text{He}^-$ ,  $\text{B}^-$ , and  $\text{Ca}^-$  ions as examples. The method that has been developed to investigate the collisional properties of negative ions with radiation will be illustrated with the results of recent measurements of the cross sections for single-photon detachment of  $\text{He}^-$  and  $\text{B}^-$  ions.

The question of how the FEL could enhance the current single-photon detachment measurements will be addressed, as will possibility of the use of the FEL in future multi-photon detachment experiments.

The authors would like to acknowledge his collaborators at the University (J. S. Thompson and J. Dellwo) and ORNL (G. D. Alton and R. N. Compton).

## Applications of Broadband FEL Cavities to Experimental Physics

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At Stanford University, the Mark III infrared free-electron laser has demonstrated broadband operation in the range of 2–8  $\mu\text{m}$ <sup>1</sup>. The wavelength was extended to shorter wavelengths by harmonic generation and third harmonic lasing. The wavelength range of 2–8  $\mu\text{m}$  could be covered by gap tuning at three different electron beam energies(see figure 1).

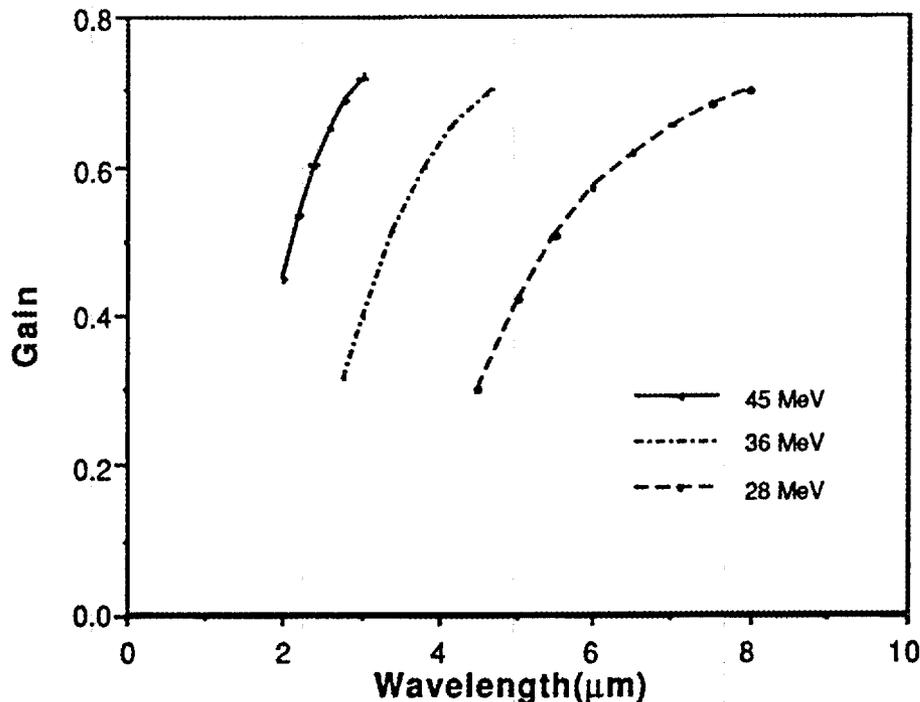


Figure 1: Gain vs. wavelength for three different electron beam energies for the Mark III FEL.

Although gain exists over a large range of wavelengths, one cannot take advantage of this fact unless the optical cavity is also very broadband. The Mark III laser uses Brewster plate output coupling and metal mirrors to allow useful lasing over the range from about 1.5 to 8  $\mu\text{m}$ . Scatter and absorption become excessive at wavelengths shorter than 1.5  $\mu\text{m}$  and the Brewster plate material used(calcium fluoride) becomes lossy at 8  $\mu\text{m}$ . The output coupling scheme is shown in figure 2. A choice of four different Brewster plates can be used in order to vary the output coupling or use different materials. Sapphire has been used and a range of output coupling from 2% to 16% has been achieved. Each plate can be rotated by  $\pm 1^\circ$  to vary the output coupling continuously.

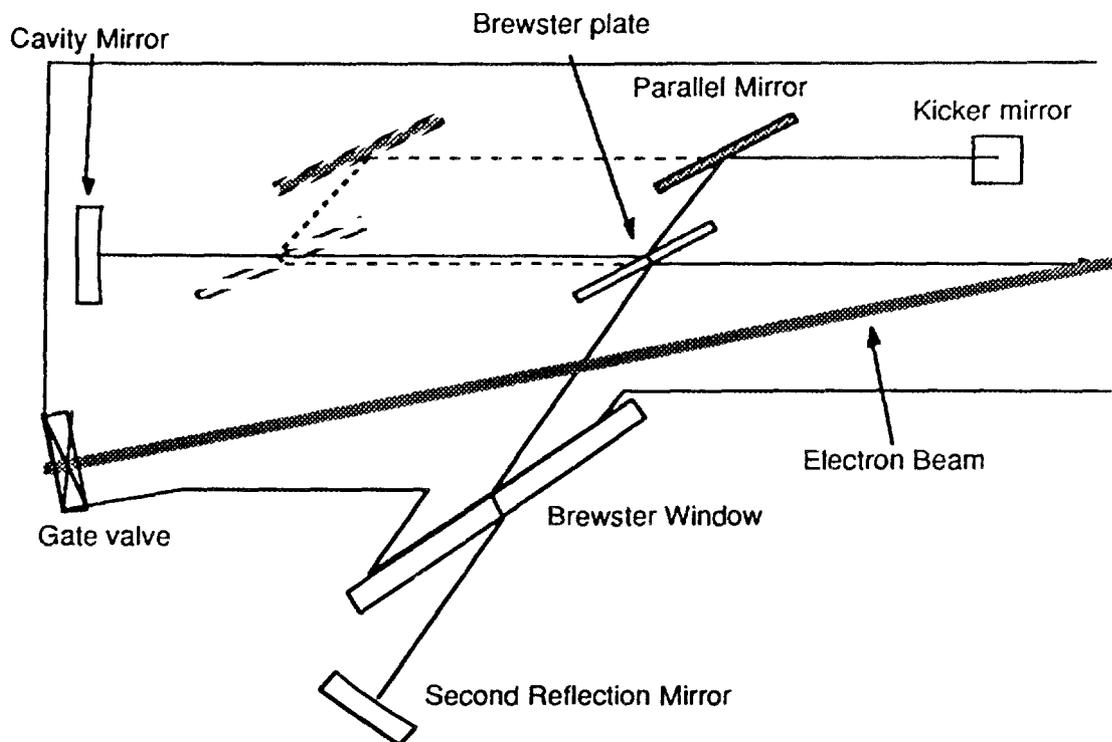


Figure 2: Broadband output coupling scheme used in the Mark III FEL.

The short wavelength limit of the Mark III is limited by the high energy limit of the accelerator which is now 44 MeV. This allows operation down to 2  $\mu\text{m}$  with reasonable power. One can get to shorter wavelengths by two means:

1.) Third harmonic lasing. This is described in an accompanying paper<sup>2</sup>. The gain is large for large wiggler parameters so the Mark III, whose maximum wiggler parameter is 1.03, is not ideal for harmonic operation. Another requirement is for excellent electron beam quality. Here, the Mark III accelerator is well suited to the task, though the energy spread still reduces the gain by a factor of two from the ideal electron beam value.

2.) Harmonic generation. Since the peak power of the laser is quite high, it is possible to use non-linear crystals to double or quadruple the light. We have used three crystals to accomplish this with encouraging results. The results are shown in Table 1. Note that the peak power is reduced by a factor of four by the nature of the output coupling. If all the light could come out in a single beam, one could get much better conversion efficiency. This might be accomplished by some sort of interferometric outcoupler on a plate with an AR coating on one side. The AR coating would not have to be extremely broadband since only the wavelength region between 2  $\mu\text{m}$  and 4  $\mu\text{m}$  would be doubled. One key issue is whether the AR coating could handle the high intracavity

fluences. Another problem is the possibility of zero output coupling if one of the mirrors is moved to the destructive interference point.

Table 1. Frequency doubling results using the Mark III IRFEL beam.

### HARMONIC GENERATION RESULTS

CRYSTAL	AgGaSe <sub>2</sub> (1&2)	LiNbO <sub>3</sub>	β-BaB <sub>2</sub> O <sub>4</sub>
DIMENSIONS (cm)	Rectangular 1x1x2 long	Cylindrical 1x3 long	Rectangular .5x.5x0.8long
PHASEMATCHING ANGLE (degrees)	1) 90 2) 52.5	45	22
FUNDAMENTAL WAVELENGTH (μm)	1) 3.15-3.27 2) 3.78-4.2	1.98-2.48	0.99-1.24
SECOND HARMONIC WAVELENGTH (μm)	1) 1.58-1.64 2) 1.9-2.1	0.99-1.24	0.495-0.620*
ENERGY CONVERSION EFFICIENCY	1) 17-41% 2) 7-10%	10-50%	1-10%
TEMPORAL WALKOFF (psec/cm)	1) -2.28 2) -0.77	-0.072	2.7
BIREFRINGENT WALKOFF (degrees)	1) 0 2) 0.64	1.93	2.9
COATING	1) AR coated 2) uncoated	AR coated	uncoated

\* Note the second harmonic wavelength for β- Barium Borate is the fourth harmonic of the FEL. Quadrupling the FEL from 1.98-2.48 μm down to 0.495-0.620 μm using LiNbO<sub>3</sub> and β-BaB<sub>2</sub>O<sub>4</sub>.

The energy per pulse at short wavelengths is limited by mirror damage. Silver on diamond turned copper offers the highest damage threshold we have measured. Extracavity damage thresholds have been measured at as low as 90 J/cm<sup>2</sup> for a 2.8 μsec pulse. The damage threshold is very sensitive to spot size however and our best estimate from intracavity damage is 40 J/cm<sup>2</sup> normalized to a 1 μsec pulse. Using this value, it is possible to calculate the maximum average power at 60 Hz for various length cavities. This have been done in figure 3 for the case of a 2.5 meter long cavity. The Rayleigh range is 55 cm in this case.

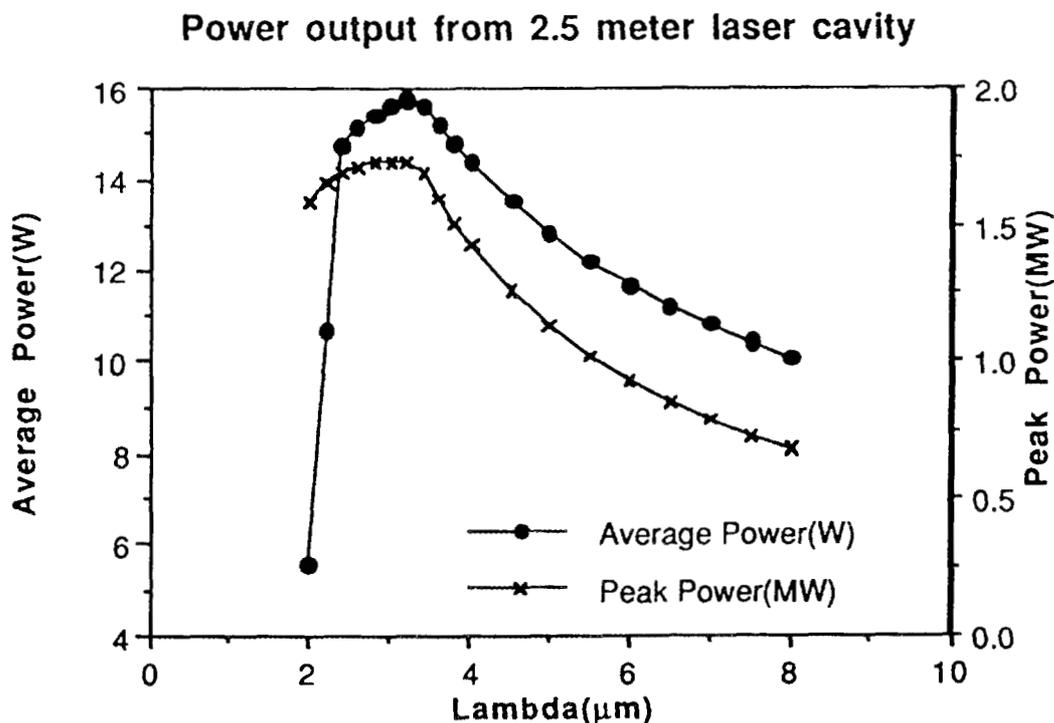
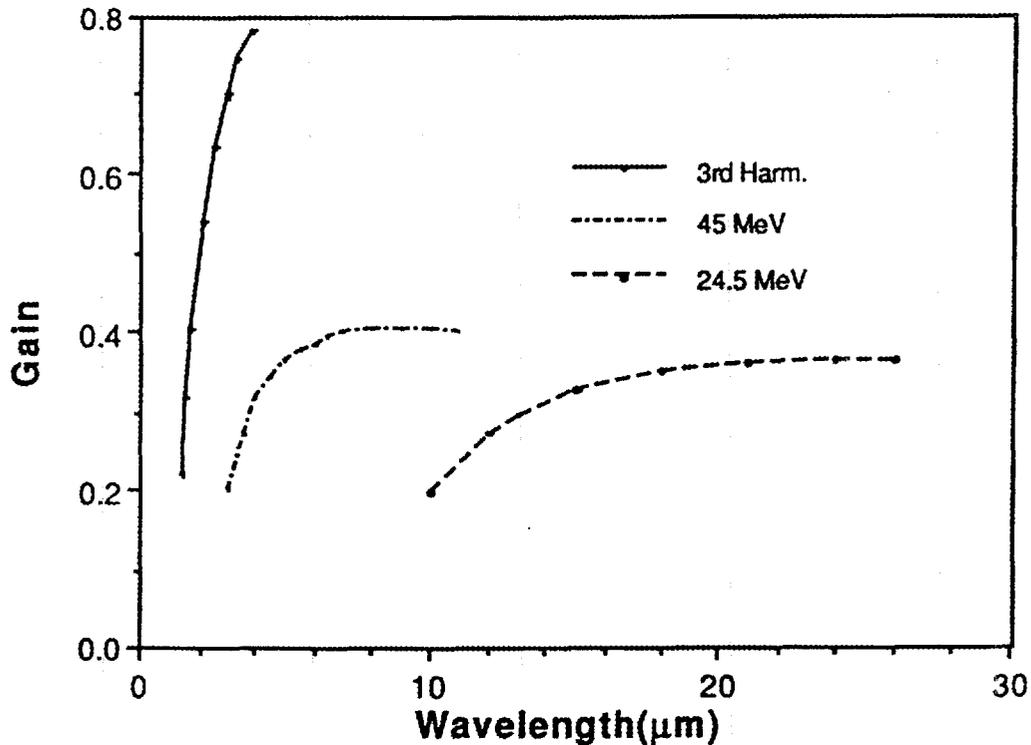


Figure 3. Peak and average power at 60 Hz calculated for the Mark III with a 2.5 meter cavity and 55 cm Rayleigh range. Only two of the four outcoupled beams are included in this.

On the long wavelength side, the problem is with Brewster plate materials. Although zinc selenide is transparent out to about 15 μm, it has much too low a damage threshold for most purposes. Failure of ZnSe Brewster plates in the Mark III has indicated a damage threshold of about 6 J/cm<sup>2</sup> for a 1 μsec. macropulse. The mirrors fail at a fluence ten times this value. Halide materials are transparent to quite long wavelengths and have quite high damage thresholds but are very sensitive to radiation damage. If a material is found the optical bore limits the wavelength to about 10 μm.

One obvious fact from the data in figure 3 is that the power falls off as the wavelength is lengthened. This is due to the lower electron beam energy. This can be improved upon by using a wiggler with higher wiggler parameter and longer wavelength. This also opens the optical bore and allows low diffractive losses out to about 30 μm. The shorter wavelength range can still be covered by harmonic lasing or external harmonic generation. This gain vs. wavelength for a 33 period undulator with 3.6 cm period is shown in figure 4. The wavelength range of 1 to 28 μm could be covered using only two energy settings. The problem of how to outcouple the power at

wavelengths greater than 8  $\mu\text{m}$  still needs to be solved. Some sort of unstable resonator might be the solution, but the analysis still need to be done for this.



**Conclusion:** The free-electron laser is capable of extremely broadband operation. Metal mirrors allow reasonable cavity Q from 1  $\mu\text{m}$  out to the far infrared. Optical bore size can be large enough to operate out to about 30  $\mu\text{m}$  if the period is sufficiently long. Damage thresholds are a problem at the short wavelength end. This might be solved by new materials or by new cavity designs. Output coupling is more of a problem. Transparent materials with high damage thresholds are extremely difficult to find at wavelengths longer than 8  $\mu\text{m}$  and transparent materials of any kind are difficult to find at wavelengths longer than 20  $\mu\text{m}$ . The best solution at short wavelengths may be harmonic generation. Interferometric outcoupling may be a good way to improve conversion efficiency. High average power doubling still needs to be demonstrated.

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<sup>1</sup>S. V. Benson, J. Schultz, B. A. Hooper, R. Crane, and J. M. J. Madey, Nucl. Inst. and Meth. in Res. A428F, (1987)

<sup>2</sup>S. V. Benson and J. M. J. Madey, Phys. Rev. A 39, (1989) 1579

## INFRARED FREE ELECTRON LASERS IN CONDENSED MATTER RESEARCH

Free Electron Lasers (FEL's) have been demonstrated as sources of *intense and tuneable* radiation in the infrared and far infrared parts of the electromagnetic spectrum. In the far infrared range, FEL's do not have competition from conventional sources, since by and large the conventional sources are fixed in wavelength. In the IR range, tuneable light is available through a succession of nonlinear optical processes following a conventional source, but at the expense of the loss of much power and stability. The combination of wide tuneability in a single source, short pulse duration, good stability, high peak power and an extremely large average power has made infrared FEL's a unique source of radiation for condensed matter research. In the past year, three different experiments have used the capabilities of an infrared FEL for the first time in nonlinear optics and dynamical studies of condensed matter. In each study the infrared FEL has been used as a tuneable, high peak power laser pump.

The Mark III infrared FEL used in these studies is continuously tuneable from 2 to 8  $\mu\text{m}$ . <sup>[1]</sup> Its output is in the form of a series of 1 to 8  $\mu\text{s}$  macropulses separated by 67 ms. Each macropulse contains a train of micropulses each approximately 2 ps in duration and separated by 350 ps from each other. The micropulses typically have Fourier-transform limited spectra, however, a uniform chirp can be introduced in their wavelength within the macropulse envelope. The monochromaticity of the macropulses is adequate for most studies,  $\delta\lambda/\lambda \sim 10^{-2}$ . Typical micropulse powers range from  $10^5$  to  $10^6$  watts.

In the first experiment, the Mark III was used to obtain the full spectrum of the third-order optical susceptibility,  $\chi^{(3)}(-3\omega; \omega, \omega, \omega)$ , in polyacetylene.<sup>[2]</sup> (See Figure 1) The open circles are from a previous study that used a Nd:YAG laser in conjunction with three stages of nonlinear optical processes in order to achieve "tunability".<sup>[3]</sup> However, that source left gaps in the spectrum and could not cover the important low energy region. The FEL work completed the spectrum and showed that the magnitude of  $\chi^{(3)}(-3\omega; \omega, \omega, \omega)$  reaches  $\sim 10^{-8}$  esu at 0.6 eV, the largest value of an electronic  $\chi^{(3)}$  inside the gap of a semiconductor. Two peaks at 0.6 eV and 0.89 eV in the spectrum of  $\chi^{(3)}(-3\omega; \omega, \omega, \omega)$  were assigned to three- and two-photon resonance enhancement, respectively, implying that states of opposite symmetry lie near the 1D band gap at  $E_g \sim 1.8$  eV.<sup>[2]</sup> These results are an important test for recently developed free-electron<sup>[4]</sup> and highly correlated<sup>[5]</sup> models of nonlinear optical response in polyacetylene.

In the second experiment, the Mark III was used to selectively pump the vibrational band of submonolayers of adsorbed butane on an  $\text{Al}_2\text{O}_3$  surface.<sup>[6]</sup> The polarization dependence of the desorption rate showed that the adlayer is butane in an all-trans configuration with the carbon backbone perpendicular to the surface. The desorption dynamics point to a thermal mechanism in which vibrational energy deposited in the C-H stretching bonds causes resonant heating of the butane adlayer and subsequent thermal desorption.<sup>[6]</sup>

In the third experiment, time resolved spectroscopy was used to test applicability of Davidov's proposal for energy transport in  $\alpha$ -helix to acetanilide, (ACN), a model molecular crystal.<sup>[7]</sup> The picosecond time structure of the micro-pulses, the large average power and the wave length stability of the Mark III was

important to the success of this experiment. In this work the dynamics of the anomalous  $1650\text{cm}^{-1}$  band of ACN crystals was investigated by time resolved bleaching experiments. It was found that the ground state recovery time of this vibrational excitation is  $15 \pm 5$  picoseconds; too short to be of any significance in transport of energy over macroscopic distances. Furthermore, this anomalous band that appears on cooling of ACN,<sup>[8]</sup> persisted after rapid pulsed heating. It is suggested that the controversial  $1650\text{cm}^{-1}$  band is associated with a structural phase transition which can be kinetically suppressed and not with a self-trapped vibrational excitation.

These experiments appear to open the door for the *infrared* FEL's to play a unique role where intense and tunable source of infrared radiation is needed.

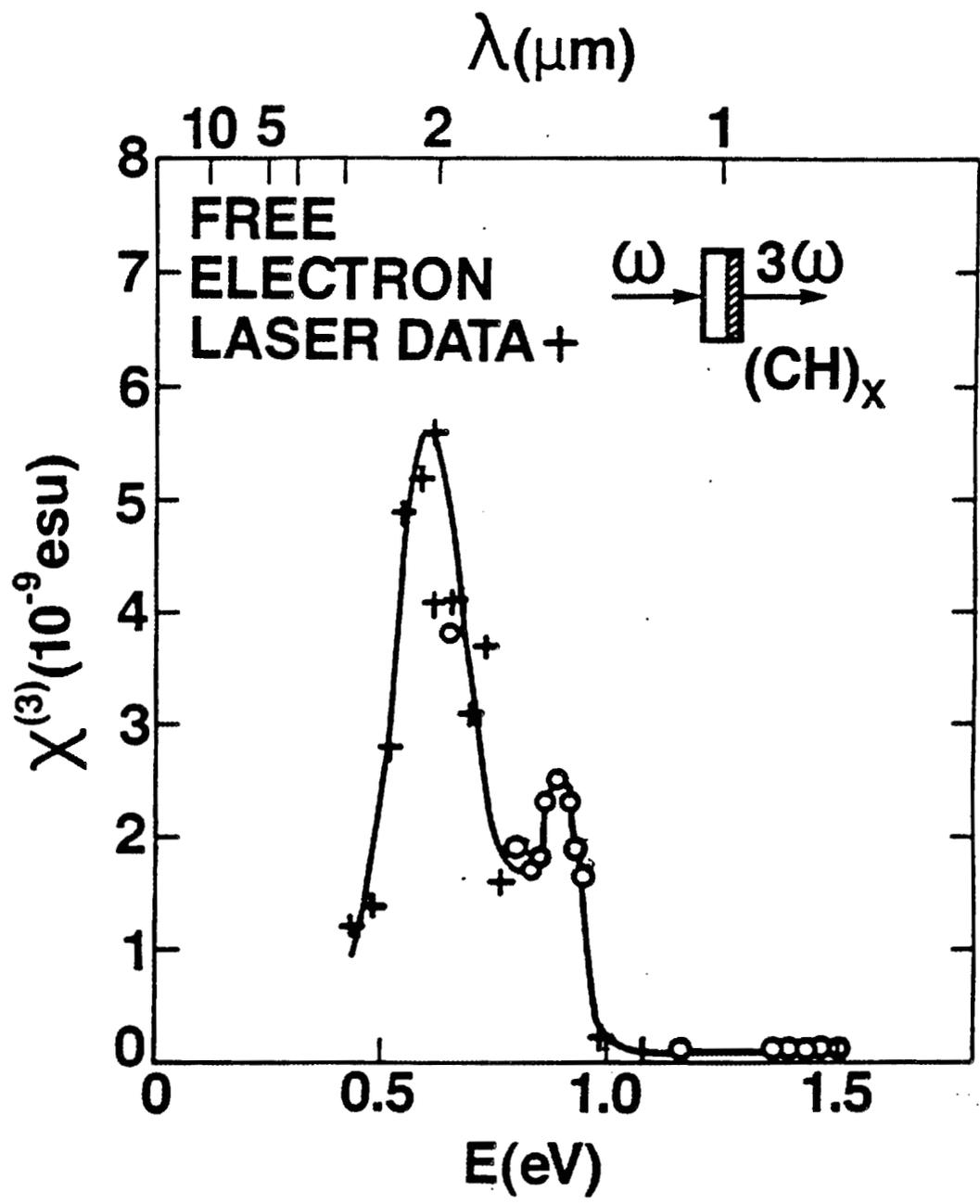
Shahab Etemad

Bell Communications Research

Figure 1. The  $\chi^{(3)}(-3\omega; \omega, \omega, \omega)$  spectrum in *trans*-(CH)<sub>x</sub>; (+) free electron laser data, (O) from Ref. 3.

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#### 4. CONCLUSIONS

The main conclusions of the workshop can be summarized as follows:

1. In the IR region (between 3 and 15 micrometers) there are no other sources of coherent light presently available, which can compete with an FEL source.
2. The combination of an FEL source of coherent light with conventional lasers will be a valuable tool for the performance of "pump-probe" (two-color) experiments.
3. Present day RF-Linac driven FEL's can cover the region between 1 micron and 40 microns. By either internal harmonic generation or frequency doubling crystals, one can reach the 250 nanometers region (UV-region).
4. ORNL researchers in the atomic and molecular fields were mostly interested in the IR region, whereas those involved in condensed matter studies would use the UV region to study electronic transitions.
5. After a much lively round-table discussion, the consensus was that an FEL facility, if available, would promptly run out of beams to satisfy the expected high demand by users in material science, biophysics, and industrial applications.



## APPENDIX



## APPENDIX

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