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COMBUSTION DYNAMICS FACILITY

**April 1990 Workshop
Working Group Reports**

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TABLE OF CONTENTS

Workshop Agenda	i
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I Introduction and Summary	3
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II Working Group Reports

A. Photoion-Photoelectron Processes	9
B. Intramolecular Dynamics and Primary Dissociation Processes	13
C. Clusters and Ionic Beam Processes	17
D. Spectroscopy, Energetics and Dynamics of free Radicals	27
E. Surface and Condensed Matter Processes	31
F. Combustion Dynamics	43
G. IRFEL Technology	51
H. ALS Beamline Technology	63
I. Theory of Computational Requirements	67

III Appendix A	
Attendees List	77

COMBUSTION DYNAMICS FACILITY WORKSHOP

April 5-7, 1990

Lawrence Berkeley Laboratory

Bldg. 50 - Auditorium

AGENDA

Thursday, April 5

Plenary Session I

N. Phillips, Chairperson

CDF INITIATIVE

8:30 a.m. - 8:40 a.m.	Welcome	C.V. Shank
8:40 a.m. - 8:50 a.m.	Washington Perspective	R.S. Marianelli
8:50 a.m. - 9:30 a.m.	CDF Overview	Y.T. Lee
9:30 a.m. - 10:00 a.m.	CDF/SNL	J.S. Binkley
10:00 a.m. - 10:30 a.m.	Coffee Break	

Plenary Session II

A. Kung, Chairperson

FACILITY

10:30 a.m. - 11:00 a.m.	Users Program	C.B. Moore
11:00 a.m. - 11:30 a.m.	IRFEL	K.J. Kim
11:30 a.m. - 12:00 p.m.	ALS Beamline	M.G. White
12:00 p.m. - 12:30 p.m.	Lasers and Experimental Stations	A.H. Kung
12:30 p.m. - 1:30 p.m.	Lunch	

Plenary Session III

M. El Sayed, Chairperson

SCIENTIFIC PROGRAM

1:30 p.m. - 2:30 p.m.	Intramolecular Dynamics and Primary Dissociation Processes	Y.T. Lee
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2:30 p.m. - 3:15 p.m.	Metal and Semiconductor Clusters	R.E. Smalley
3:15 p.m. - 3:30 p.m.	Coffee Break	

Plenary Session IV	SCIENTIFIC PROGRAM	
3:30 p.m. - 4:15 p.m.	Non-linear Optical Study of Materials	Y.R. Shen
4:15 p.m. - 5:00 p.m.	Free Radical Reactions in Combustion	F. Tully
5:00 p.m. - 5:45 p.m.	Photoelectron and Photoion Processes	T. Baer
6:00 p.m. - 7:00 p.m.	Reception (LBL Cafeteria)	
7:00 p.m. -	Dinner	

Friday, April 6

Special Session

M. White, Chairperson

8:30 a.m. - 9:00 a.m.	Synchrotron Experiments in ORSAY	I. Nenner
9:00 a.m. - 9:20 a.m.	Status of the ALS	J. Marx

Parallel Working Group Sessions

9:20 a.m. - 9:30 a.m.	Charge to Working Group	N. Phillips
9:30 a.m. - 10:15 a.m.	Question and Answer on Facility Performance Capabilities	
	K. J. Kim, Chairperson	
10:15 a.m. - 10:30 a.m.	Coffee Break	
10:30 a.m. - 12:30 p.m.	Working Groups: presentation and discussion of ideas	

Working Group Sessions

- A. Photoelectron-photoion Processes (Bldg. 70A, Rm. 3377)
Irene Nenner, Chairperson
 - B. Intramolecular Dynamics and Primary Dissociation Processes (Bldg. 70, Rm. 191)
Richard Zare, Chairperson
 - C. Cluster and Ionic Beam Processes (Bldg. 50B, Rm. 4205)
Mike Bowers, Chairperson
 - D. Spectroscopy, Energetics, and Dynamics of Free Radicals (Bldg. 50A, Rm. 5107)
James Weisshaar, Chairperson
 - E. Surface and Condensed Matter Processes (Bldg. 50A, Rm. 5123)
Giacinto Scoles, Chairperson
 - F. Combustion Diagnostics (Bldg. 50A, Rm. 5104)
Terry Cool, Chairperson
 - G. IRFEL Technology (Bldg. 50D, Rm. 116)
Steven Benson, Chairperson, Roger Miller & John Goldstein, Co-Chairpersons
 - H. ALS UV Beamline Technology (Bldg. 70A, Rm. 3377)
John West, Chairperson
- 12:30 p.m. - 1:30 p.m. **Lunch**

- 1:30 p.m. - 4:00 p.m. Working Groups: Continued discussion, begin specification of facility and experimental stations, report preparation
A. through H.
I. Theory and Computational Requirements (Bldg. 50A-5132)
A. Wagner, Chairperson
- 3:00 p.m. - 3:30 p.m. **Coffee Break**

4:00 p.m. - 5:00 p.m. Panel Question and Answer Period on
 Users Program (Bldg. 50 Auditorium)
Panel members: J.S. Binkley, G. Fisk, R. K. Johnson
 A.H. Kung, Y.T. Lee
Special Guest: A. H. Laufer

Saturday, April 7

8:30 a.m. **Report by Working Group Chairpersons**
 D. Neumark, Chairperson

15 minute talk and 5 minute discussion each:

8:30 a.m. - 8:50 a.m.	Group A (I. Nenner)
8:50 a.m. - 9:20 a.m.	Group B (R. Zare or substitute)
9:20 a.m. - 9:40 a.m.	Group C (M. Bowers)
9:40 a.m. - 10:00 a.m.	Group D (J. Weisshaar)
10:00 a.m. - 10:30 a.m.	Coffee Break
10:30 a.m. - 10:50 a.m.	Group E (G. Scoles)
10:50 a.m. - 11:10 a.m.	Group F (T. Cool)
11:10 a.m. - 11:30 a.m.	Group G (S. Benson)
11:30 a.m. - 11:50 a.m.	Group H (J. West)
11:50 a.m. - 12:10 p.m.	Group I (A. Wagner)

12:10 p.m. - 12:20 p.m. Workshop Summary Y.T. Lee

12:20 p.m. **Adjourn**

I Introduction and Summary

This document summarizes results from a workshop held April 5 – 7, 1990, on the proposed Combustion Dynamics Facility (CDF). The workshop was hosted by the Lawrence Berkeley Laboratory (LBL) and Sandia National Laboratories (SNL) to provide an opportunity for potential users to learn about the proposed experimental and computational facilities, to discuss the science that could be conducted with such facilities, and to offer suggestions as to how the specifications and design of the proposed facilities might be further refined to address the most visionary scientific opportunities.

Some 130 chemical physicists, combustion chemists, and specialists in UV synchrotron radiation sources and free-electron lasers (more than half of whom were from institutions other than LBL and SNL) attended the five plenary sessions and participated in one or more of the nine parallel working group sessions. Seven of these sessions were devoted to broadening and strengthening the scope of CDF scientific opportunities and to detail the experimental facilities required to realize these opportunities. Two technical working group sessions addressed the design and proposed performance of two of the major CDF experimental facilities. These working groups and their chairpersons are listed below. A full listing of the attendees of the workshop is given in Appendix A.

Working Group	Chairperson
A. Photoion and photoelectron Processes	I. Nenner
B. Intramolecular Dynamics, and Primary Dissociation Processes	R. Zare
C. Cluster and Ionic Beam Processes	M. Bowers
D. Spectroscopy, Energetics, and Dynamics of Free Radicals	J. Weisshaar
E. Surface and Condensed Matter Processes	G. Scoles
F. Combustion Diagnostics	T. Cool
G. Infrared Free Electron Laser (IRFEL) Technology	S. Benson
H. Advanced Light Source (ALS) UV Beamline Technology	J. West
I. Theory and Computation	A. Wagner

Plans for a comprehensive users program were also presented, and user comments were noted. Attendees reacted favorably to these plans, and a suggestion made during the workshop to empanel a Users Organization for the CDF has already been acted on.

This document serves as a record of each working group's findings and recommendations. The output of the scientific working groups was integrated with research opportunities previously identified in a separate document, entitled CDF Scientific Program Summary (LBL PUB-5284), published in June 1990.

PUB-5284 also contains a full description of the management plan and operations plan of the CDF as a national user facility. Highlights from the scientific discussions at the workshop are presented below, as are major facility recommendations. The reader is urged to consult PUB-5284 for a complete description of the facilities and research proposed for the CDF.

SCIENTIFIC HIGHLIGHTS

This workshop was the most recent in a series of workshops and reviews starting in 1986 that have examined research opportunities in chemical dynamics and combustion chemistry. Many promising lines of research had been discussed and described in some detail before this workshop convened. Therefore, for some working groups (groups A, B, and D), the focus was on equipment needs and experimental chamber design: the lists of experiments that had already been proposed were only slightly updated. In other cases, groups outlined and discussed significant new avenues of research.

The Photoion and Photoelectron Processes working group fully endorsed the promise of high-resolution threshold photoelectron studies, PEPICO studies, and studies of molecular excited states. New suggestions include exploring the utilization of higher-energy photons than previously considered. Examples include the preparation of diatomic and polyatomic di-cations, whose spectroscopy and reactivity could then be explored for the first time, and PEPICO studies of ion-molecule reactions involving excited-state O^+ and OH^+ .

The Working Group on Intramolecular Dynamics, and Primary Dissociation Processes likewise benefitted from extensive previous discussion of experimental possibilities at the CDF. The group affirmed the promise of the infrared multiple-photon excitation (IRMPE) technique to probe the dissociation dynamics of the ground electronic potential energy surface and of studying molecular processes in combustion using the femtosecond laser system at the CRF. In addition, the group proposed the new possibility of using the IRFEL to prepare and explore unique and previously inaccessible regions of the electronically excited potential energy surfaces.

The Working Group on Cluster and Ionic Beam Processes built on previously described research possibilities to develop a new and wide-ranging experimental program. The

main elements of this program are spectroscopic studies of clusters based on the IRMPE technique, studies of cluster energetics (including determinations of ionization potentials, bond energies, and lowest-energy pathways), and studies of the reaction dynamics of small ionic clusters.

The Working Group on Spectroscopy, Energetics, and Dynamics of Free Radicals echoed the promise of previously described experiments to extract properties of gas-phase free radicals and unusual species using IR-VUV double resonance techniques involving the IRFEL and ALS beamlines. They emphasized the importance of developing techniques to produce high fluxes of internally cold free radicals and of focusing the studies on species that are prominent in gas-phase free-radical spectroscopy in which the combination of the ALS, the IRFEL and the advanced lasers of the Chemical Dynamics Research Laboratory (CDRL) would serve as a "universal free-radical spectrometer."

The Working Group on Surface and Condensed-Matter Processes refined and substantially expanded the experimental program that had been previously put forward. The elements of the research now proposed include a comprehensive study of photodynamics and chemical dynamics at the vacuum-surface interface, spectroscopic and dynamical studies at interfaces using nonlinear optical techniques, dynamical studies in solution, hole-burning spectroscopic studies, and dynamic optical studies of electronic states in semiconductors.

The Working Group on Combustions Diagnostics not only affirmed the importance of experiments that can be strictly described as pertaining to "combustion diagnostics," such as laser-based point measurements in turbulent reacting flows and the development of advanced femtosecond laser-imaging techniques, but also emphasized the synergism of such experiments with fundamental studies. The group recognized the scientific values to combustion diagnostics of chemical dynamics studies of elementary reactions, spectroscopic studies of reactive intermediates, and studies of chemical kinetics and energy transfer. The group also proposed that thought be given to a facility for the study of soot and smoke, and to the study of toxic combustion.

A seventh working group discussed the role of theory and computation in the CDF. Above all else, they emphasized the importance of an interactive relationship between theorists and experimentalists in developing a fundamental understanding of molecular structure and chemical reactivity, and in producing predictive simulations of real-world combustion problems. Important new opportunities that were identified by this group for the CDF include, at the molecular level, calculation of potential energy surface for electronically excited states; characterization (vibrational spectroscopy, PES, photodissociation, and ionization) of aromatic compounds, radicals, clusters, and gas-surface interactions; quantum chemistry beyond three atoms and associated sensitivity analyses. On the modeling and simulation level, the group recommended comprehensive studies of soot formation, NO_x processes, and coal combustion, to augment studies in turbulent flow.

MAJOR FACILITY RECOMMENDATIONS

There were numerous recommendations to improve the proposed facilities. The major recommendations are highlighted here. Additional details and recommendations are in the working group reports which constitute the remainder of this report.

The IRFEL working group, in general, endorsed the baseline design. It made several suggestions for improvements and emphasized the need for developing details of a feedback-feedforward scheme and for investigating methods to efficiently couple out the IRFEL energy. Several scientific groups stressed the need for improved wavelength stability and resolution.

The ALS Beamlines working group was supportive of the current design. It recommended performing ray-tracing calculations for both the undulator beamline and the bend magnet beamline to fortify the current analysis. The group suggested that the CDF provide for photons at energies higher than 30 eV, further develop functional schemes for order suppression and develop means to handle corrosive chemicals in the beamline environment.

The scientific groups considered several different experimental station designs to match the proposed science. Each station would consist of an experimental chamber, plus a variety of source chambers, detectors and associated lasers for use with the IRFEL, ALS, and advanced laser systems. Maximum compatibility of components among different experimental stations was seen as a most important aspect. At least eight different types of main chambers were proposed (see the working group reports for descriptions).

These groups endorsed the proposed advanced laser systems and stressed the importance of having enough picosecond lasers to handle the many experiments proposed to synchronize the ALS pulses and/or IRFEL pulses with laser pulses. They recommended having one staff scientist per experimental station to guide the operation and maintenance of the stations.

The theory and computation group made important suggestions regarding the visitors program and staffing needs to match the scientific opportunities proposed by the group. For computation, the CPU equivalent of an 8-processor Cray YMP was recommended.

II Working Group Reports

A. PHOTOION-PHOTOELECTRON PROCESSES

Group Members

Tom Baer (Liaison)
George Gabor
Jan Hessler
Erik Johnson

Joe Berkowitz
Ed Grant
Steve Hulbert
Irene Nenner (Chairperson)

Photoionization experiments have been discussed in most previous workshops. The ideas outlined in the CDF Scientific Program Summary Draft are good.

NEW EXPERIMENTS DISCUSSED

A. Measuring Ions

Ed Grant's idea of measuring TPES of positive ions in order to get dication spectra. This is a very interesting, exciting, new but difficult, experiment. It should definitely be included under TPES. The main drawback is that most ions to be investigated would require higher energy photons than presently planned.

B. Investigations of Ion-molecule Reactions

Chuek Ng mentioned PEPICO investigations of ion-molecule reactions with such species as O^+ (2D , 2P) or $OH^+(v)$ with various neutral collision partners. The trick here is to prepare O atoms and OH free radicals and then prepare the ions in selected states by PEPICO. These processes are important in plasma chemistry where lots of excited species are present. No such experiments have been done because it requires very high intensity sources and efficient methods for free radical generation. The CDF is the ideal location for such experiments because free radical production will be one of the main thrust areas.

EQUIPMENT REQUIRED

A. Beam source chamber

A differentially pumped molecular beam source chamber with at least a 5000 l/s net pumping speed in the main chamber and a 1000 l/s pumping speed in the second chamber is required. This chamber should be useable as both a normal cold gas source as well as a cold free radical source.

B. Large experimental chamber

Main experimental chamber large enough to hold a short TOF/reflection mass spectrometer, a quadrupole mass filter, a hemispherical electrostatic energy analyzer, an ion trap and a fluorescence detection system. Each of these items would be mounted on a flange and could be dropped into the chamber from one port or another. The main chamber should be pumped by a 1000 l/s pump with a separately pumped beam dump. This list may have to be modified in order to accommodate the need for portability as well as compatibility with other chambers in the CDF. Maximum compatibility is highly desirable.

C. Lasers

The lasers required for these experiments are as follows:

1. cw/psec visible dye laser system synchronized with the ALS.
2. cw-high resolution IR laser. This could be an F-center laser or the equivalent (future technology). The IR-FEL especially with the high resolution FT mode will also be very valuable.
3. A 1000 Hz Excimer/dye laser system for triggering with zero energy electrons.
4. A 1000 Hz Excimer (ArF) for photolysis and radical preparation.

D. Electronics

The electronics were not discussed, but there was enough information about this from previous communications and the discussion with George Gabor of LBL. The key is to have 100 psec resolution per channel in signal detection.

MONOCHROMATOR FOR THE BENDING MAGNET PORT

Everyone agrees that we should not write off the high energy experiments. Everyone also agrees that higher orders in the photon beam can kill certain experiments and cause serious problems with data interpretation on nearly all experiments. No one came up with a solution that would allow us to extend the energy range to 100 eV and at the same time be able to operate with high resolution, high flux, and no higher orders between 10 and 25 eV. It appears that these requirements are simply incompatible. Finally, the outside experts also concur that scanning the undulator may not be possible on day one.

It will, however, be possible to tune over the 2.2 % band pass of the undulator and scan in this fashion. This means that we can scan over about 20 Å at 750 Å. Assuming a band pass of 0.015 Å (.3 meV) [resolution of 50,000], and 5 points per 0.015 Å interval, we can scan about 6,600 points. Such a scan would take 4 hours at 2 sec per point. This is just about the lifetime of one injection, after which the undulator gap could be changed. Thus for high resolution scans, this mode would be just fine. However, if we redo the calculation for a resolution of 0.1 Å (2.2 meV) photon resolution, the same scan would take only 30 minutes. What do we then do during the rest of the ALS fill cycle? The latter "low resolution" mode will be extremely important for high quality survey TPES at resolutions not previously obtained.

Most of the experiments related to combustion studies, e.g. TPES of free radicals, PEPICO studies, free radical IR spectra, etc. require the low energies. Given the above arguments, duplication on the bending magnet port is preferable. However, it is important to outfit a second bending magnet port for future expansion with a grazing incidence monochromator that will let us go to 150 eV. Both of these beam lines would be located on the ALS floor.

B. INTRAMOLECULAR DYNAMICS AND PRIMARY DISSOCIATION PROCESSES

Group Members

Laurie Butler
Fleming Crim (Co-chairperson)
Carl Hayden
Yuan Lee (Liaison)
Frank Tully
Rick Woodin
Dick Zare (Chairperson)

Hao Lin Chen
Dave Golden
Bill Jackson
Jane Rice
Alec Wodtke
Tony Young

The following are additions to the information that is in the draft of Scientific Summary, distributed before the workshop, written about intramolecular dynamics and photodissociation (see LBL Pub.-5284, editor).

NEW EXPERIMENTS

The IRFEL is potentially a useful, powerful, preparative tool for exploring unique regions of the electronically excited potential energy surfaces. Vibrationally mediated photodissociation experiments, in which a second photon dissociates a highly vibrationally excited molecule prepared by vibrational overtone excitation, have shown that excitation from the vibrationally excited state reaches regions of the excited potential energy surface that are otherwise inaccessible.* Using the IRFEL could extend the approach, which has been restricted to excitations involving light atom stretching motions, to include lower frequency, large amplitude motions. For example, exciting one or a few quanta of bending vibration with the IRFEL might produce good Franck-Condon factors for excitation to linear electronically excited states that are inaccessible from ground vibrational states. Such experiments could reveal new bound excited states and could produce unique dissociation dynamics.

*M.D. Lika, J.E. Baggott, A. Sinha, R.L. Vander Wal, and F.F.Crim, J. Chem. Soc. Faraday Transactions II 84,1483 (1988).

PROPOSED EQUIPMENT

The hardware requirements for these experiments go well beyond the ALS and IRFEL. They include the advanced laser (the Fourier transform limited VUV laser) and, at the CRF, the femtosecond laser system. In addition, the experiments require a set of conventional lasers and several vacuum chambers (end stations) of varying sophistication. It seems that a number of the proposed experiments require a relatively modest vacuum chamber with a versatile, differentially pumped source and an interaction chamber with fluorescence, ion time-of-flight, and electron time-of-flight detection. This type of chamber will have means of introducing light from conventional lasers, the advanced laser, the ALS, and the IRFEL for both preparation (initial excitation) and detection. It can accommodate a large variety of experiments requiring a single molecular beam and multiple light sources. To use the resources of the CDRL efficiently, two of these should be available for alternate experiment preparation and use. It is likely that many features of this modular apparatus are similar to those required by other types of experiments, and it may be possible to arrive at a design with many standard elements since this apparatus will be simple enough to modify easily. It is clear that a set of interchangeable sources is essential to these experiments.

A more elaborate apparatus for crossed molecular beam scattering experiments and for acquiring angular distributions in photodissociation measurements should be part of the proposed facility. This apparatus is likely to be three to four times more expensive than the modular apparatus and will certainly require more sophisticated maintenance and oversight. The two fundamental choices are a fixed source apparatus with a rotating detector and a rotating source apparatus with a fixed detector. The rotating detector configuration offers great flexibility in the sources, as they are relatively unconstrained by size and pumping requirements, but have the limitation that introduction of light into the detector for optical detection is difficult to the point of being impractical. The rotating source configuration provides great versatility in detection, since the detector is fixed, but less flexibility in the sources. The best course of action is to provide a machine of each type, and, while construction of both for the set of experiments proposed here may be impossible, use of an existing rotating source apparatus from Professor Lee's laboratory and the construction of a new fixed source apparatus is a feasible approach. These devices serve some of the most elaborate experiments proposed for the facility. The goal is to perform reactive scattering experiments that obtain angular distributions on state selected species using optical preparation and, in many cases, optical detection techniques.

Some of the people at the workshop imagine being able to come to use the scattering apparatus without any special need for the ALS, IRFEL, or advanced laser. Rather, they imagine using conventional lasers and this machine.

The conventional lasers are essential to doing interesting science in the CDRL. The picosecond laser that is synchronized to the ALS and IRFEL is essential to their use for molecular dynamics research. Not all of the wavelengths available are so unique that they are of compelling interest without the timing capabilities of the ALS or IRFEL. Thus, the synchronized picosecond lasers are very important. The advanced laser system producing Fourier transform limited vuv light is another capability that, because of its cost and complexity, will be available to many workers only in the CDRL. The versatile femtosecond laser system at the CRF falls in the same category although it will not be part of the CDRL, excimer lasers for photolysis, probably one operating on F and one on Cl, and a CO₂ laser for exciting molecules to dissociation once lasers as well. The technology is evolving, but today good choices are an excimer laser pumped dye laser that is frequency doubled, a pair of frequency doubled dye lasers pumped by an injection seed Nd:YAG laser that is synchronized to the IRFEL macropulses at 50 Hz, and a continuous ring dye laser for use with, among other things, the ALS operating as a quasi continuous source. All of these lasers require the usual auxiliary hardware and optics.

C. CLUSTERS AND IONIC BEAM PROCESSES

Group Members

Michael Bowers (Chairperson)
David Chandler
James Farrar
Fred Grieman
Mark Johnson
Rick Smalley

Philip Brucat
Mostafa El Sayed
George Fisk
Martin Jarrold
Dan Neumark (Liaison)
Rob Whetten

The group held wide ranging discussions on the various kinds of research possibilities using the unique facilities available at the Chemical Dynamics Research Laboratory (CDRL). Also discussed were the types of machines needed to carry out the research. What follows is a brief summary of our discussions. No attempt has been made to make this a scholarly document with references to the open literature such a document would require. Rather, it is a report of the workshop that reflects the collective judgement of those in attendance.

PROPOSED SCIENCE

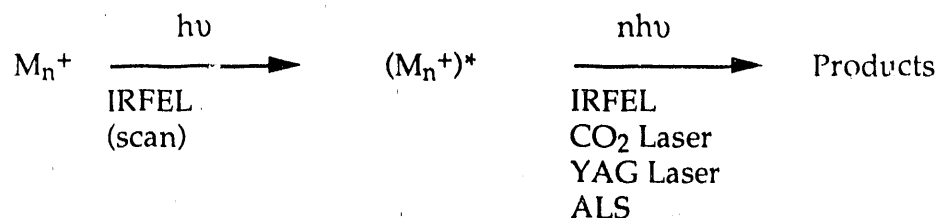
The field of gas phase cluster research is exploding at present with essentially every top research institution involved in a significant way. Perhaps the principal fuel for this explosion is the desire to understand the physical and chemical properties of this new form of matter at a fundamental level. Of perhaps equal importance, however, is the hope, and expectation, that clusters will solve some long standing problems in catalysis and combustion and may lead to dramatic discoveries in micro electronic properties of materials. It is this synergistic combination of the fundamental and practical that makes research in this area so exciting.

In this report three principal areas of cluster research will be highlighted: spectroscopy, energetics and dynamics. The work proposed will be almost exclusively on ionic systems. There are tremendous advantages in studying ions because they can be easily transported, mass selected, stored in traps and detected. Many of the studies will directly give information on conjugate neutral systems and for many properties, such as

cluster binding energies or cluster reactivity, ionic and neutral systems give essentially the same results. What follows are very brief summaries of the experiments we wish to pursue.

A. Spectroscopy

Despite the tremendous interest in clusters at the present time, very little is known about the most rudimentary spectroscopic properties of these species. The availability of the IRFEL with a basic range of 200 to 3300 cm^{-1} and the possibility of doubling to extend the range to 6000 cm^{-1} opens the door for vibrational spectroscopy on a wide range of cluster species. The method and initial systems we intend to study are given below.



When the first photon strikes a resonance, absorption of further IRFEL photons will be greatly enhanced leading to product fragmentation as the detection method. Other photon sources will be used to enhance detection as required.

The symbol M_n^+ symbolizes any of the clusters we wish to investigate:

Systems (M_n^+):

carbon: C_n^+ , C_n^- , C_n , O_m^\pm , $C_n H_m^\pm$, etc.

metals (oxides, carbides, nitrides, etc.)

semiconductors

mixed metals or semiconductors

alkali halides

physisorbed adducts on clusters

chemisorbed adducts on clusters

reaction intermediates

The emphasis initially will be on smaller systems ($n < 20$) but there is no intrinsic reason larger systems could not be studied. Both ion beam and ion trap instruments will be used, each having its particular advantages. (These instruments will be briefly described at the end.)

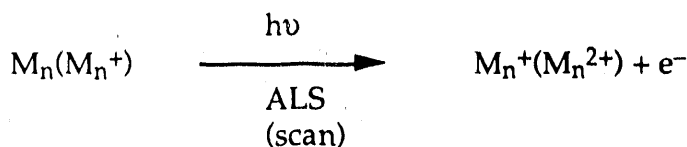
Perhaps the most important and interesting systems listed above are the various carbon and carbonaceous clusters because of their potential importance in combustion. Also of practical interest are the physi- and chemisorbed adducts as these systems should be very revealing regarding the catalytic properties of small metallic particles.

Neutral clusters can be studied using the same general methods. In this case the products need to be detected via ionization using either an F₂-excimer laser or preferably the ALS. Great care will have to be taken to assure the products come from the cluster of interest and not from higher clusters since the neutral beam will not be mass selected.

B. Energetics

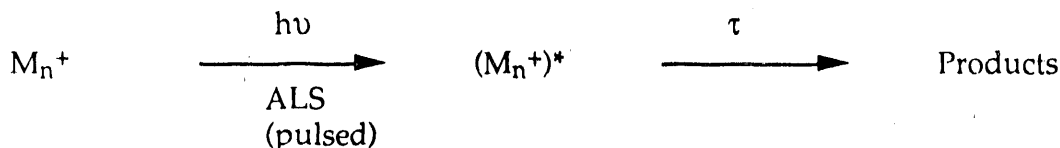
Three kinds of experiments are envisioned. These will be discussed in order. The systems listed in section I.A. above will also be of importance here. Again M_n or M_n^+ will represent any one of these systems.

Ionization Potentials



In this experiment a beam of cluster neutrals or mass selected ions is ionized using the ALS. Several methods can be used to obtain the ionization potentials. In the first, the product ion is observed as the ALS is scanned, and the threshold for ionization determined. In the second, the photoion and photoelectron products are determined in coincidence as the ALS is scanned. Again a threshold is determined. Finally, the ALS can be set at an energy above threshold and the photo emitted electrons energy analyzed. Each method has its strengths and weaknesses. In all of them "cold" clusters are required and great care need be given to eliminate hot band contributions. The instrument required will be either a neutral/ion beam apparatus, a TOF machine or a hybrid of the two. These numbers are extremely important for characterizing the structure and stability of the various cluster systems and measuring them will receive a high priority in our initial experiments.

Bond Energies



In this experiment a mass selected ion beam is irradiated with a pulse of photons from the ALS. The energized cluster then takes a characteristic time to decompose. This lifetime will depend most strongly on the energy of the bond being broken. Consequently, the arrival time distribution of the ionic fragment at the detector can be modeled using RRKM theory, with the binding energy as a variable parameter. These

determinations can be done at several photon energies to assure consistent results are obtained. The ALS is essential for such experiments on larger clusters due to large kinetic shifts in these systems and the necessity for the fragmentation to take place on the microsecond timescale.

At present the primary method for obtaining thermochemical data of this kind is measurement of endoergic energy thresholds by collision induced decomposition. This is a useful method for small clusters but many factors, especially the kinetic shift, eliminate this method for n above about 8-10. Hence, the ALS based photodissociation techniques will be the only methods available for measuring these crucial numbers.

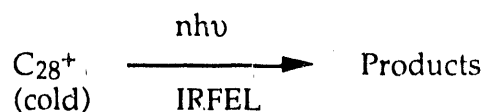
Finally, when the ionic bond dissociation values are coupled with the ionization potentials, a simple thermodynamic cycle allows determination of the neutral bond dissociation values. The method described here is in fact the only way these important neutral binding energies can be determined.

Lowest Energy Pathway

When energized particles dissociate, often a number of reaction products are observed. It is very useful to know the energy ordering of these product asymptotes even if exact dissociation energies cannot be measured. A case in point is the fragmentation of small carbon clusters. For example

			%
	→	$C_{25}^+ + C_3$	20
	→	$C_{23}^+ + C_5$	15
$(C_{28}^+)^*$	→	$C_{18}^+ + C_{10}$	36
	→	$C_{14}^+ + C_{14}$	29

energized C_{28}^+ undergoes metastable loss of C_3 , C_5 , C_{10} and C_{14} , all with significant intensities on the 10 - 30 μs time scale. The sequential energy onsets of these competing reaction channels can be determined



by irradiating cold C_{28}^+ in an ion trap using the IRFEL. At low fluences the first product to appear will correspond to the lowest energy path. As the power is increased the photon absorption rate will overcome the dissociation rate of the lowest energy channel and the second onset will appear. With careful variation of laser power, and some luck,

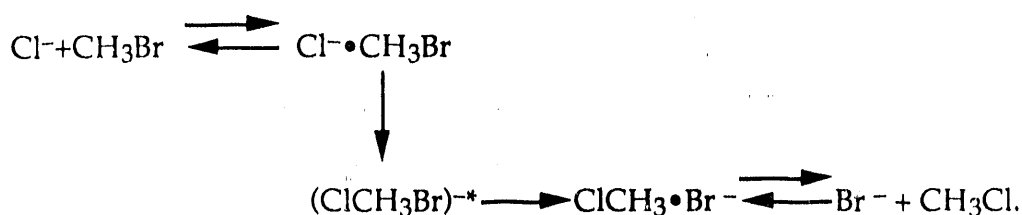
all of the onsets could be established. Similar examples occur in many systems of interest.

C. Reaction Dynamics

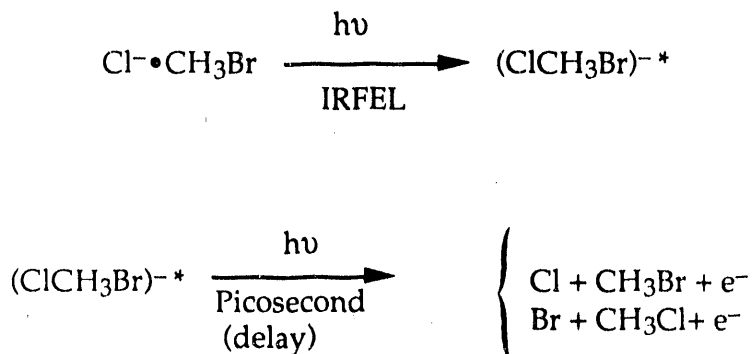
There are a very wide range of reaction dynamics studies that can be pursued using the unique facilities of the CDRL, and many such experiments were discussed by our working group. Only very brief summaries of a few experiments will be given.

Reaction Complexes

One of the most important organic chemistry reaction mechanisms is the SN2 mechanism. An example of such a reaction is

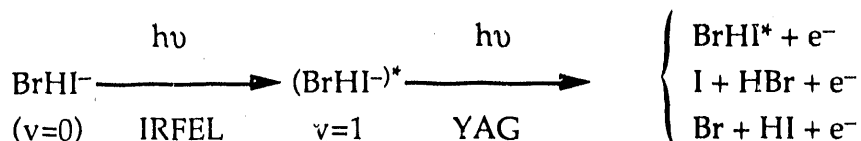


The electrostatically bound cluster $\text{Cl}^- \cdots \text{CH}_3\text{Br}$ can be readily formed in a nozzle expansion source. The IRFEL can be used to probe the vibrational spectrum of the adduct using methods described earlier. The rate limiting transition state for the overall reaction is the quasi-symmetrical species $(\text{ClCH}_3\text{Br})^-*$, where the methyl group is planar. The energy of this transition state can be determined by observing the onset of the Br^- signal as the IRFEL is scanned. An interesting dynamics experiment also is possible



The observed photoelectron spectra should be a strong function of the delay time for the second photon since the character of the initial $(\text{ClCH}_3\text{Br})^{-*}$ photoexcited intermediate will rapidly be changing with time as the system starts to cross the transition state. These changes will be reflected on the conjugate neutral surface accessed by the second photon. Interpretation of the time dependence of the photoelectron spectrum should reveal many details about the dynamics in the region of the transition state.

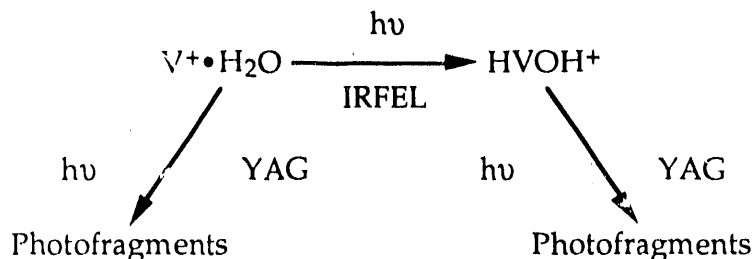
A second type of experiment is also proposed.



The BrHI^- ion is only weakly bound and $v = 1$, in the antisymmetric stretch, samples the surface much nearer the dissociation asymptote than $v = 0$. Consequently, when the system is transported to the upper (neutral) surface by the second photon, dramatic effects are expected in the product distribution relative to the $v = 0$ system; specifically $\text{HBr} + \text{I}$ is expected to become the dominant channel instead of $\text{HI} + \text{Br}$. These changes can be readily extracted from the photoelectron spectrum for $v = 1$, and compared to theoretical predictions.

Isomerization Barriers

An example of the determination of an isomerization barrier was given earlier. A second, much different example is given here.



When vanadium ion is clustered to water, two forms are possible; the "electrostatic" complex $\text{V}^+ \bullet \text{H}_2\text{O}$ and the "inserted" molecule HVOH^+ . These two structures can readily be distinguished by their very different laser photofragment spectra. The pure electrostatic complex can be formed in 100% purity in a jet expansion. This complex is irradiated by the IRFEL and the photofragment spectrum monitored. The onset of the HVOH^+ spectrum indicates the photoexcited $\text{V}^+ \bullet \text{H}_2\text{O}$ complex has isomerized, and analysis will yield the isomerization barrier.

INSTRUMENTATION

As our discussion took place it became apparent that at least three separate instruments were required in order to accomplish the most important experiments. Brief descriptions of these instruments follow.

A. Ion Beam Machine

In this instrument ionic clusters will be made either in continuous or pulsed jet expansion sources, mass selected by a quadrupole, deflected into an octapole ion guide/trap where they can interact with photons from the IRFEL, ALS or various lasers, are then deflected into another quadrupole-mass filter and finally detected using single ion counting methods. The primary functions of this instrument will be determination of binding energies of clusters or ligated clusters and in vibrational spectroscopy of smaller cluster systems where dissociative detection can occur on the sub millisecond time scale. This instrument will also be used for ionization potential measurements where the detected particle is the product ion. For measurement of first ionization potentials the cluster source will have to be aligned coaxially with the ALS.

B. Tandem Time of Flight

In this instrument cluster ions will be made in a pulsed source and injected into the first stage TOF for mass selection and spatial ion focusing. Photo beams will then interact with the mass selected cluster at the spatial focus yielding either photoelectrons, ionic photofragments or both. Consequently two different TOF devices will be accommodated at the focal point: a photoelectron TOF out-of-plane and a reflectron TOF in-plane for photofragment detection. Numerous ports will be available throughout the device for irradiation of the ions by the various light sources. This instrument is required for all of the photoelectron spectroscopy experiments and some of the spectroscopy experiments. It will be designed in such a way that it can be readily reconfigured to accommodate specific requirements of a given experiment. For example, the electron TOF unit could follow the reflectron TOF instead of precede it or it could be located on axis with the first TOF to analyze fragments that are allowed to pass through the reflection field.

C. ICR Ion Trap

This instrument will use a custom laser desorption pulsed cluster ion source for external injection into an ion trap enclosed by a 7-10 Tesla superconducting magnet. Ion detection, ejection and energizing will be accomplished by a state of the art fast Fourier transform electronics and associated computer system. Provision will be made to initially cool the ICR cell/vacuum system to 77 K with eventual cooling to 4 K.

This instrument will be essential for much of the vibrational spectroscopy and for the lowest energy pathway experiments. This device can also be used to "chemically" prepare certain clusters in situ which can then be interrogated using the IRFEL, ALS or both. Conversely, photochemistry in the ion trap can be used to prepare exotic ions whose chemistry can then be probed.

D. Lasers

All of the experiments described here will utilize either the IRFEL, the ALS or both. In most cases, additional "conventional" lasers will also be required to generate the ions, do double resonance on them, or to assist in their detection. Those lasers required for the work described here are listed below.

1. 1000 Hz Excimer Laser (cw cluster generation)
2. 50 Hz YAG/DYE Laser
(photofragment spectroscopy)
(photoelectron spectroscopy)
(pulsed cluster generation)
3. High Power Pulsed CO₂ Laser
(multiphoton dissociation)
4. F₂ Excimer Laser (product ionization)

In addition, an effort should be made to increase the resolution of the IRFEL for spectroscopic studies. One suggestion for doing so is

5. IR Interferometer
(for FEL output)

The lasers will also need special carts designed and constructed to allow transport and to position them for the various experiments. An extensive inventory of optics, optical mounts, laser dyes and other optical accessories will be required as well.

E. Cost

The three required experimental stations will take about \$1,200,000 to construct. In addition, approximately \$500,000 will be needed for the lasers, optics, dyes and other accessories. Obtaining support of this magnitude for the initial equipment complement seems eminently reasonable when the total cost of the building, IRFEL, and our share of the ALS is taken into account. Further, it is anticipated that a significant number of the very best research groups in the country will be involved in carrying out this work. The

success of the entire enterprise will depend very strongly on how much money is initially allocated to construct the experimental stations.

One additional area of concern must be voiced. If real instruments that incorporate state of the art design are to be constructed, then substantial funding must be made available at the design stage, to allow oversight of the construction and to bring the instruments on line. Ion beam/ion optic technology is complex and the detailed requirements of each of the three instruments are substantial. Working instruments simply will not appear unless this requirement is met.

D. SPECTROSCOPY, ENERGETICS AND DYNAMICS OF FREE RADICALS

Group Members

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Robert Perry
Jim Weisshaar (Chairperson)

Free radical experiments have been discussed in previous workshops. There are no additions to the energetics and dynamics sections in the draft CDF Scientific Program summary. New ideas were developed in studying the spectroscopy of gas-phase free radicals and are discussed below.

SPECTROSCOPY OF GAS-PHASE FREE RADICALS

The availability of the ALS and the IRFEL in conjunction with conventional laboratory laser systems provides exceptional new opportunities for measurement of ionization potentials and IR absorption spectra of gas-phase free radicals. Adiabatic ionization potentials of radicals are key ingredients in many thermodynamic calculations of bond energies and reaction energetics, but AIP's are often poorly known. The infrared absorption spectroscopy of gas phase radicals is still poorly developed due to the difficulties of creating radicals in good number density, detecting the absorption spectrum and identifying the spectral carrier. IR absorption spectra, even at 2-5 cm^{-1} resolution, can provide important structural information and a critical test of quantum chemical calculations. Rotationally resolved, higher resolution spectra will yield detailed geometric information and assignments of narrow spectral lines for *in situ* laser diagnostics. The combination of the ALS, the IRFEL, and state-of-the-art laboratory lasers can reasonably be called a "universal free radical spectrometer."

Resonant two photon ionization (R2PI) with one photon in the infrared region (ω_{IR}) and other in the VUV (ω_{UV}) can provide sensitive detection of IR absorption and attach a mass label to the spectral carrier. The radical source will utilize IRMPD or UV photolysis or pyrolysis in a supersonic expansion. Chen and co-workers have recently demonstrated a continuous pyrolysis source of vinyl and ethynyl radicals producing

number densities of 10^{14} cm^{-3} at the nozzle and $>10^{10} \text{ cm}^{-3}$ in a skimmed beam 30 cm downstream.

First, the photoion yield curves (mass-selected parent or fragment cation current vs ω_{UV}) of free radicals will be measured by crossing a VUV photon beam at 7-11 eV (either the ALS or a laboratory source) with the beam of internally cold radicals. In favorable cases of modest geometry change between radical and cation, the parent cation yield curve will provide an accurate adiabatic ionization potential. Detection of threshold photoelectrons vs ω_{UV} can provide cation vibrational spectra as well.

Next, survey IR absorption spectra with $2\text{-}5 \text{ cm}^{-1}$ resolution will be obtained using the IR + UV R2PI technique with ω_{IR} scanned and ω_{UV} fixed. The IRFEL provides ω_{IR} and the laboratory laser system provides ω_{UV} ; the pulse structures of these systems are well matched. Mass-selected cation yield vs ω_{IR} constitutes the IR absorption spectrum. We estimate $10^4\text{-}10^5$ cations/sec in this mode. Judicious choice of ω_{UV} and of the cation detected will maximize discrimination between $v = 0$ and $v = 1$ radicals and minimize background signals. There are two ways to proceed. We can use the parent cation yield curve to set ω_{UV} just below the threshold for ionization of $v = 0$ and detect parent cations. This will succeed if symmetry permits ionization from $v = 1$ of the radical to $v^+ = 0$ of the cation, (as is usually the case in polyatomic radicals) and if the Franck-Condon factor $|\langle v = 1 | v^+ = 0 \rangle|^2$ is sufficiently large. The technique will be most sensitive to those radical vibrations that carry the radical geometry towards the cation geometry. Alternatively, we can use a fragment cation as detector and set ω_{UV} just below the corresponding appearance potential. This will succeed as long as the energy in $v = 1$ of the radical becomes available for dissociation of the parent cation, as is usually the case in polyatomics. In either case, the tunability and narrow bandwidth of the VUV photon is crucial.

For high resolution, rotationally resolved spectra ($\sim 10^{-3} \text{ cm}^{-1}$), we will combine a cw F-center laser ($\sim 10 \text{ mW}$ in the IR) with the ALS, using the latter as a μ VUV source. Signal estimates are $10^3\text{-}10^4$ cations/sec in this mode.

In limited cases, laboratory lasers alone have accomplished the same goal of radical IR absorption spectra in specific wavelength regions. Typical IR lasers cover specific wavelength regions and are not suitable for survey spectra. The beauty of the IRFEL is its ability to smoothly scan over the entire "chemical infrared", from 200 cm^{-1} to 6000 cm^{-1} (using frequency doubling crystals at the upper end). In the far IR, where large amplitude motions can be studied, there are no competing laser sources (see below). Survey spectra from the IRFEL will obviate the search problem inherent in high resolution work.

The unique combination of IRFEL, ALS, and laboratory lasers allows us to launch a comprehensive program in the IR spectroscopy of unstable species cooled in supersonic expansions. Species of particular interest include hydrocarbon radicals such as ethynyl, vinyl, ethyl, and propargyl as well as small organometallic species such as partially

ligated transition metal atoms. The generality of the IR-UV resonance ionization detection will be limited primarily by the experimenter's ingenuity in designing radical sources. This is a wide-open area of endeavor whose exploration has been hampered in the past by the need to custom design a laboratory technique for each radical of interest.

INSTRUMENTATION

Free-radical experiments at the CDRL require a radical source chamber, an intermediate chamber for differential pumping, and an interaction chamber where the radical beam intersects photon beams and where charged particles are detected. The source chamber should be evacuated by a 1500-cfm Roots blower to permit formation of continuous beams using the pyrolysis source. The intermediate chamber requires a trapped 10-inch diffusion pump, and the interaction chamber should be turbo-pumped. Cryoshielding and light baffling will be important in minimizing background signals. The interaction chamber should include a TOF mass spectrometer, which can drop in from the top flange, and an electron impact ionization-quadrupole mass spectrometer for beam diagnostics on the molecular beam axis.

Since this apparatus has much in common with those proposed for other areas of research, standard designs will be advantageous for common components.

The most useful conventional laser systems include (i) a kilohertz excimer laser (F_2 , KrF , or ArF), (ii) a high-power pulsed CO_2 laser, (iii) one or more high-repetition-rate pulsed dye lasers, and (iv) a high-resolution cw IR laser, such as an F-center laser.

E. SURFACE AND CONDENSED MATTER PROCESSES

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INTRODUCTION

We have identified three main themes within which new exciting chemical dynamics research could be carried out. This research could have a substantial impact on problems which are central to the Department of Energy mission, i.e. to ensure that the research base of the country in fields such as combustion, catalysis and, in general, energy production and utilization shall remain healthy. We note that, if the present trend of limited support for individual investigators, combined with the difficulty of funding large facilities in fields such as chemistry that traditionally have not used this modus operandi continues, the likelihood that the above-named research base shall remain healthy, is not going to be very high.

The three themes which we have identified are:

A. State-to-state chemical dynamics at the vacuum-surface interface

For the sake of simplicity, this theme will be discussed in two parts. In the first we propose a series of experiments in which the translational, rotational and vibrational states of the products of a chemical reaction, or of an inelastic collision between a molecule and a surface are measured in a much more complete way than has been possible so far. The second will deal instead with the photophysics and photochemistry of absorbed molecules where analogous full quantum state characterization shall be carried out. Both types of experiments are feasible in the same single experimental facility, which is described at the end of this report. Both types of experiments draw photons from both the IRFEL and ALS sources.

B. Non-linear optics probing of dynamics at interfaces

In this type of experiment, the interface between two dense phases shall primarily, but not exclusively, be probed. At least one of the two phases needs to be transparent to the probing photons. These techniques show great potential for probing dynamics in "real life" situations (solution interfaces or atmospheric pressure gas/solid interfaces). They all need, of course, the high power levels of the proposed IRFEL source.

C. The study of molecular conformation and finite size effects by means of hole-burning spectroscopy

These experiments straddle a broad range of phases: from gas phase clusters, to supported clusters, to bulk solid state systems. They all have in common the use of the IRFEL for efficient pumping of narrow portions of the vibrational spectrum of these materials. Molecular manipulation in solids and the study of mesoscopic materials is essential to many areas of modern technology due to the ever increasing trend towards smaller and smaller devices.

DESCRIPTION OF THE PROPOSED RESEARCH

A. State-to-State chemical dynamics at the vacuum-surface interface

Gas-Surface collisions

Molecular beam scattering from surfaces is a powerful experimental tool for studying the dynamics and kinetics of the interaction of molecules with surfaces. The recent coupling of surface science, molecular beam and laser technologies has made possible the measurement of total energy disposal and redistribution in gas-surface scattering (i.e. the quantification of translational, vibrational, rotational and electronic energies). The rapid development of non-linear optical methods for generating high intensity, pulsed vacuum ultraviolet laser radiation makes the outlook for state-resolved studies of a wide variety of inelastic and reactive collision processes extremely promising. To date, the molecules NO, H₂, N₂, CO, HCl and NH₃ have been scattered from surfaces with state-to-state specificity. The near-transform-limited tunable advanced nanosecond laser system at the CDRL will undoubtedly extend quantum-state-specific detection to a broader class of molecules through the development of new (2+1) and (1+1) multiphoton ionization spectroscopies. The detection of collision induced vibrational excitation in large molecules (C_n hydrocarbons) may be possible by a two-color (1+1) ionization scheme in which tunable IR from the IRFEL is scanned across a $v'' = n$ to $v' = n+1$ absorption and a fixed VUV photon from either the ALS or the advanced nanosecond laser ionizes population in $v' = n+1$.

In virtually all state-to-state scattering studies to date, the initial state distribution was determined by the relaxation of internal degrees of freedom attendant with cooling during supersonic beam formation. This technique is very useful for preparing a beam of molecules in the rotational and vibrational ground state. If the scattering dynamics of excited initial states (e.g. vibrations) is of interest, these states must be prepared by excitation of the incident molecular beam prior to its collision with the surface. The intensity and tunability of the IRFEL make it an ideal excitation source for preparing intense pulsed beams of a wide range of vibrationally excited molecules. Stimulated emission pumping using the advanced nanosecond laser will be useful in preparing pulsed beams of highly vibrationally excited molecules even if the molecule is not infrared active (e.g. H_2).

For monitoring the effectiveness of the vibrational pumping by the FEL and characterizing the distribution of the energy contents of the molecule (in the case of multiphoton pumping) the most effective method (the use of which is proposed here) is that of optothermal, bolometric, detection. The presence in the apparatus of this type of detector, will greatly facilitate the characterization of the adsorbed phases by means of low energy He atom diffraction.

The presence of a high vibrationally excited beam of molecules will instead make possible the study of their reaction and its velocity and angular dependence with organic thin films of the self-assembled type. These films have been recently shown to have atomically smooth surfaces (about one hundred lattice spacings) and offer the added advantage of remaining clean under normal (10^{-7} torr) vacuum conditions without requiring the very low pressure levels (10^{-11} torr) that are the most common requirement of surface scattering experiments. The fixed orientation of the resonant species offers unique opportunities here for the field of organic stereochemistry.

Finally, let us consider dissociative chemisorption which is the starting point for most of surface chemistry. For a diatomic molecule, this elementary step involves breaking only one intramolecular bond and forming two new bonds to the substrate. Often dissociative chemisorption occurs at a negligible rate even though dissociation is thermodynamically favored, indicating that the process is kinetically limited by an activation barrier for dissociation. Recent molecular beam studies in which the dissociation probability is determined as a function on incident translational energy have proved extremely useful. However, important issues concerning the relative efficacy of translational vs. vibrational energy in surmounting the activation barrier have been largely unexplored. By extending the translational activation studies to include highly vibrationally excited molecular beams, these issues can be addressed. The intensity and relatively long (100 μs) macropulse length of the IRFEL should enable relatively large fluxes of vibrationally excited pulsed molecular beams with variable translational energy to be produced. The broad tunability of the IRFEL will be extremely useful in the study of larger molecules such as hydrocarbons since it will allow the excitation of both high frequency C-H stretch and lower frequency skeletal bending motions to be excited.

Relevance to combustion

The great majority of combustion processes of practical importance occur in the presence of walls and/or two phases, i.e. in the presence of interfaces (including the interface with clusters). It follows that progress in the chemical dynamics at interfaces of radicals and other species relevant to combustion (hydrocarbons, CO, etc.) can have a substantial impact on the whole field. Furthermore, the reactions of oriented (self-assembled) hydrocarbon and other functionally substituted organic surfaces with free radicals (H, O, OH, etc.) shall significantly add to our knowledge in this area. Free radicals of interest to combustions can also be deposited on relatively inert substrates by slow ion deposition and studied *in situ* by both atom scattering and electron spectroscopic methods.

B. Photodynamical studies at the vacuum-surface interface

Surface processes will be induced and explored using the IRFEL, ALS, and auxiliary lasers, so as to understand basic bond breaking/making and energy transfer process on surfaces, and in some specific cases to help understand important practical applications of photons in driving surface processes. The proposed experiments described below can be divided into two categories: vibrational energy driven surface processes; and photoelectronic driven energy and charge-transfer driven surface processes.

Vibrational-energy driven surface processes

Bond breaking and making at surfaces are so intimately connected to the bond vibration coordinate, that the thorough investigation of the latter is crucial to the understanding of most chemical dynamics processes including, of course, those of interest to combustion. Cavanagh (NIST) and Harris (AT&T Bell Labs), and their coworkers, have (among others) recently shown the range of expected vibrational lifetimes on surfaces. In ps and fs pump/probe experiments, they found relaxation rates from 100's of picoseconds on dielectrics to as short as 6 fs. Also demonstrated was the sensitivity of the rates to the local vibrational and phonon environment and, on metals, to electron mediated coupling.

The first experiments will explore the simplest questions: what are the rates and modes of relaxation of a vibrationally excited adsorbate, and can this induce interesting surface processes? IRFEL-induced desorption of adsorbed molecules, especially hydrocarbons, could be the way to start these first experiments. In this case the initially excited bond must eventually couple to the vibrational coordinate that moves the entire molecule away from the surface, (a type of predissociation).

Recently the IR-induced desorption of butane from Al_2O_3 surfaces was explored using the FEL laser at Stanford. It was observed that butane desorbs via a one photon IR adsorption, when the FEL is resonant with a C-H vibration (within the 15 cm^{-1} bandwidth). By doing isotopic substitutions, and coadsorbing other molecules, it was shown that absorption of the IR photon by a neighboring molecule can desorb a nontargeted molecule.

The new IRFEL will allow single and multiphoton IR desorption studies on insulators and graphite, and single photon desorption (when possible) on metals. Its high power and broad tunability are essential. Measurements of the decrease in surface coverage, as monitored by thermal desorption spectroscopy, He atom specular reflection, or surface spectroscopy (such as UPS) after exposure to the IR is a sensitive measure of the efficiency of the coupling of the initially excited bond into the final desorption coordinate. Single IR-photon induced desorption are only possible when the photon energy (plus any thermal internal energy of the molecule) exceed the binding energy to the surface. Linearity with laser fluence indicates a net desorption/deexcitation time which is too short for adsorption of a second photon. The quantum yield will determine the relative rates of desorption vs. relaxation. Sublinear power dependence indicates long lifetimes and saturation.

If the power dependence is higher than the first order, a multiphoton IR process is clearly indicated. By splitting and recombining the IRFEL laser, one can adjust the relative spacings of the nearest pairs of micropulses from 0 to 16 ns. This measures the time over which the previously adsorbed photon can still add to the multiphoton process.

In the gas phase, vibrationally excited molecules have been shown to predissociate weakly adsorbed adducts, such as noble gases or other molecules. Thus in analogy: A monolayer (or more) of an adsorbed molecule will be covered with a submonolayer of He or Ne, the sample cooled to 4 K. The desorption of the rare gas after adsorption of an IR photon by the underlying molecule will signal the transfer of energy into the desorption coordinate.

When the species desorbed is a molecule, it will carry with it, via its final vibrational and rotational states, a great deal of information. The intensity of the IRFEL allows a rapid enough desorption rate that the internal states of the desorbed molecules can be determined by the advanced dye laser spectroscopy system available to the facility. This is discussed more fully later on in this report.

Photoelectron driven energy and charge transfer surface processes

Photon induced chemistry on metals has been shown in recent years to proceed when the molecules are excited by the photon into an intramolecular repulsive state. The rate of dissociation to form reactive radicals is then fast enough (5 to 500 fs) to successfully compete with existing quenching mechanisms. In these, charge transfer plays an important role. i.e., when the molecule is excited directly, the excited electron can simply tunnel to any available resonant substrate orbital, stopping the chemistry. Charge transfer has also been used recently by several groups to promote surface reactions. In this case photons excite hot electrons (and possibly holes) in the substrate. These then transfer to the adsorbate, inducing dissociation desorption and/or reaction.

These experiments have made it very clear that surface photochemistry can be very efficient, that charge transfer processes can figure prominently in both promotion and

inhibition of the surface reactions, and that the dynamics are rich, yet accessible to the experiment. A focus for the first experiments could be to understand these processes when the species involved are chlorinated hydrocarbons. Previous work on methyl chloride on Ni, Ag, Pt, and GaAs has already shown both direct and charge transfer induced chemistry and quenching. The studies at the CDRL would initially focus on the nature of the charge transfer (and other) quenching channels, and their dependence on the electronic structure of the substrate.

As the photon energy is increased, the possible photochemical mechanism for an adsorbed chlorohydrocarbon should progressively include: hot substrate photoelectron dissociative attachment to the adsorbate (observed), valence excitations of the adsorbate to known internally repulsive states (observed), hot hole chemistry, dipolar repulsive states, core hole induced reactions, and so on. To explore any but the first two, tunable UV beyond 6 eV is required. ALS will provide these photons. At 3×10^{14} photons/s, at tightest possible focus, a flux of 10^{19} photons/s/cm² is possible. Since the typical cross sections for photochemistry are about 10^{-19} cm², this implies that nearly full photolysis might be expected in times on the order of 1 s. The spectral dependence, as it correlates to the onset of allowed processes, should give immediate information on which of them are operative.

The presence of quenching in many cases can be detected simply by turning it off. By placing the adsorbed molecules on 1 or more monolayers of inert spacers, the quenching can often be gradually eliminated.

As the fastest expected quenching channel, charge transfer, should be very sensitive to the resonances between adsorbate and substrate orbitals, comparison of the above results for several different substrates should be extremely informative.

The femtosecond dynamics which leads to dissociation is typically in competition with charge transfer processes which occur on the same time scale. This curve hopping should lead to very interesting changes in the internal state of any fragments that are ejected into the gas phase. The internal states of the ejected hydrocarbon and halogen radicals could be explored using the state resolved capabilities of the proposed system.

Relevance to combustion

Surface processes in the presence of intense radiation are found in several combustion processes. Photodecomposition of halogenated hydrocarbons is essential to the study of the disposal of toxic waste. Photoconversion of radiant energy is a much studied process of considerable practical importance and considerable interest to D.O.E.

C. Nonlinear optics probing of dynamics at interfaces

For (nonlinear) optical studies of surface and interface systems, the IRFEL and ALS provide clearly identifiable advantages over the presently existing light sources. The extensive frequency range of high peak power, particularly in the IR, makes nonlinear optical methods such as SFG easily applicable for the spectroscopy and structure of molecules adsorbed on surfaces or buried between surface. Furthermore, the short duration of the intense light pulses makes many pump-probe types of experiments feasible for studying relaxation dynamics of specific or interface excitations.

The list of experiments that are potentially feasible with the IRFEL and ALS include:

- a) Vibrational spectroscopy of molecules adsorbed on surfaces or buried between surfaces by Sum Frequency Generation.
- b) Probing the electronic properties at surfaces and interfaces by resonantly enhanced Second Harmonic Generation.
- c) Probing the vibrational relaxation rate by pump-probe techniques. The IRFEL pumps a molecule to an excited vibrational level; the relaxation of this excited population is probed by either SFG, CARS, or transient absorption methods.
- d) Probing the thermalization rates of probe techniques. The IRFEL pumps a molecule to an excited vibrational level; the relaxation of this excited population is probed by either SFG, CARS, or transient absorption methods.
- e) Probing the thermalization rates of vibrational or electronic excitation at surfaces or interfaces. The IRFEL or ALS provide the pumping pulses; the thermalization rates probed by second harmonic generation.
- f) Adsorbate desorption induced by mode-selective vibrational excitation. IRFEL excites a specific adsorbate vibrational mode. Would desorption occur only for the optically excited molecule or would thermalization of the photon energy desorb molecules indiscriminately?
- g) IR multiphoton excitation and dissociation of surface adsorbed molecules. ALS pulses may excite the molecules into a specific dissociative electronic state, causing the cleavage of specific bonds in the molecules.

Relevance to the fields of combustion

These proposed experiments are inspired by the desire to fundamentally understand combustion related processes at surfaces, as well as by the drive to develop new devices for efficient utilization or generation of energy. For example, deposition of carbon or sulfur particles onto metal surfaces has recently been shown to cause structural transitions in metal surfaces. The mechanism and driving forces for such processes are unknown but can be elucidated by time resolved studies using nonlinear optical techniques. Similar techniques may be used to detect the structural change in real time in epitaxially grown thin films, and to characterize the physical and chemical properties of molecules buried at the interface between two materials. New energy generation in electronic devices based on these exotic, microscopic structures may, in principle, be conceived in the future. Last, but not least, studies of energy relaxation of molecules on surfaces provide information on the surface effects on combustion processes and catalysis. How would energized molecules, such as in a combustion chamber, react on the surfaces? Can we control catalysis or reactions in chemical plants using light? What form of energy is most efficient in promoting these surface reactions, etc.?

D. The study of molecular conformations and finite size effects by means of hole-burning spectroscopy

The proposed combination of tunable, pulsed, infrared, visible and VUV photon sources at the CDRL will be useful in performing a new generation of hole-burning experiments in which the coupling between electronic and vibrational degrees of freedom can be directly explored. Transient photophysical hole-burning experiments are essential to the characterization of novel solid state materials and high surface area catalysts. The distribution of environments, which typically exists in solids and clusters, leads to inhomogeneous broadening of spectral lines. In order to understand the intrinsic properties of the system, it is necessary to study the optical spectra without this inhomogeneous broadening, and this can be accomplished by hole burning. Examples of the types of experiments which can be performed are:

- a) A hole can be burned using a visible or UV pulse, with infrared probe to see the resulting change in nuclear configurations upon electronic excitation.
- b) UV photons from the ALS can be used to ionize a cluster or a molecule, and the IRFEL can be used to probe the resulting change in nuclear configurations.
- c) A hole in the vibrational spectrum can be burned using the IRFEL, and the effect of this on the electronic spectrum can be explored.
- d) Conventional hole-burning experiments, in which the pump and probe pulses are of the same frequency range, will be greatly facilitated,

particularly by the IRFEL, because conventional laboratory based sources do not have sufficient intensity for many applications.

Examples of the types of experiments which can be performed by these methods are:

Shape and size distributions in finite semiconductor crystals

We have developed techniques to prepare finite sized crystals of many common semiconductors, and we are exploring the intrinsic optical properties of this class of materials. These crystals contain a few thousand atoms and are physically smaller than bulk exciton diameters. As a result of this "quantum confinement," the optical spectra of these clusters strongly depend on both the size and shape of the crystals. On the other hand, recent theoretical and experimental work shows that the infrared absorption frequency of these finite dielectric crystallites depends solely on the shape, not on the size of the crystals. Existing methods for preparation result in a distribution of cluster sizes and shapes, resulting in inhomogeneous broadening of the optical spectra. Combined IR/visible hole-burning experiments will allow us to separate the effects of size and shape variation on the optical spectra.

Spectroscopy of conformational changes in inorganic crystals

Hole burning with low power lasers in the IR region of the spectrum in cooled crystals leads to rotations of ions—for example, NH_3D^+ . The burning leads to a disequilibrium in the crystals, followed by reequilibration. The kinetics of both the disequilibrium and the reequilibration process are of interest. At the moment only very special crystals can be examined—and at low temperature. With the IRFEL, the same crystals could be followed at higher temperatures, for which the kinetics are orders of magnitude faster. Fixed geometry (i.e. crystalline), kinetic processes could be followed over an extremely large range of times, from hours—a present possibility—to nanoseconds—a present impossibility. IRFEL experiments would provide an extreme test of theories of kinetics in condensed phases.

Spectroscopy of localized defects in solids

Localized defects in noble metal and alkali metal halides have been studied extensively, because these defects play important roles in a variety of technologies, including the photographic process. The intrinsic properties of localized defects such as cation vacancies in the silver halides, can be studied by hole burning experiments in which one bond in the defect is excited and the subsequent vibrational motion is observed directly as a change in the infrared absorption. For these experiments the electronic pump pulse must be tunable in the 3 to 5 eV range for the silver halides. For similar experiments on defects in the alkali halides, 5 to 8 eV light is required, and it will be necessary to use the ALS as a source for the pump.

Hole burning in polymers and catalysts

Polymers are molecules that can exist in multiple conformations and thus can offer a subject of study. The molecules can be driven to various conformations by IR excitation. One example is known: polyvinyl alcohol and related polymers. By studying the

temperature dependence of these effects, models of motion, and "annealing" in polymers can be investigated.

Chemical reactions on high surface area catalysts play an important role in the combustion process. These are typically high surface area materials, in which there are distributions of chemical environments. At present, the spatial distribution of environments in these materials can be probed by solid state NMR. How these spatial distributions translate into electronic distributions is key to understanding catalysis in these systems, but is presently unknown. New techniques of hole burning which will be developed at the CRDL will allow for the first time studies of the effects of local structural environments on the electronic properties of molecules. Knowledge of the electronic environments which the molecules experience inside a catalyst will be used to understand the mechanisms by which catalysis occurs.

EXPERIMENTAL FACILITIES

Since the research proposed here appears to be of two drastically different types, two different experimental facilities shall be needed and are described here below. In addition, some instrumentation of general utility is also listed.

A. An apparatus for state-to-state dynamics at the vacuum-surface interface

A versatile state-of-the-art facility for studying state-to-state surface dynamics will make use of all three main photon sources available at CDRL, namely the IRFEL, ALS and the advanced laser systems. This apparatus shall combine, for the first time, a universal electron impact ionizer mass spectrometer detector with a photoionization TOF spectrometer and an optothermal detector.

All three detectors will be rotatable around a vertical axis. A fixed mass spectrometer detector shall also be present that makes use of the photons provided by the ALS as a source of ionization. The ion source of this detector shall be cooled down to liquid He temperature to take advantage of the much reduced background pressure under such conditions. The e-impact mass spectrometer shall identify the products of a reaction and their velocity and angular distributions. The TOF photoionization mass spectrometer will identify the molecular vibrational and rotational states while the bolometer detector will monitor the main beam pumping by the IRFEL and be used for characterizing the surface layers by means of He diffraction measurements. The other characteristics of the apparatus are listed here below.

Molecular beam source

The proposed state-to-state gas surface scattering experiments will require a triply differentially pumped molecular beam source capable of both continuous and pulsed beam operation. The source chambers will require mechanical rotating chopping wheels to temporally tailor the beam pulse and characterize the incident beam velocity distribution via time-of-flight techniques. The beam line will also require optical access where the incident beam can be excited by the laser sources described above.

UHV scattering chamber

The scattering chamber should have a base pressure below 1×10^{-10} torr and be pumped by oil-free turbomolecular pumps. This chamber should also be equipped with normal surface analytical techniques such as UPS, LEED, ion sputtering and temperature programmed desorption. Provision for both entry and exit of the various photon sources is also required.

Target manipulator and entry system

The target manipulator should be a high precision goniometer with 3 translational and 3 rotational degrees of freedom. The target must be able to be cooled to 80 K and heated to a temperature sufficiently high to clean and order the sample (>1200 K). The manipulator design should be such that targets can be exchanged without violating the vacuum integrity of either the scattering chamber or the rotatable detectors (load-lock construction). The target manipulators will be two and will rotate around an axis which will not coincide with the axis around which the detectors rotate. The latter axis will, however, cross the circumference described.

Dedicated laser system

In addition to the photon sources provided by the CDRL, the molecular beam-surface scattering apparatus should have a dedicated stand-alone nanosecond Nd:YAG pumped dye laser system with associated nonlinear optics for generating tunable radiation between 200 and 400 nm. This dedicated laser system will be employed for "routine" state-resolved detection.

B. An apparatus for nonlinear optics at interfaces

For the nonlinear optics experiments, a general purpose UHV chamber shall be needed. This chamber shall be provided with the standard analytical tools (AUGER, LEED, MASS SPEC and ION SPUTTERING) and a crystal manipulator which can be cooled down to liquid N₂ temperatures.

Furthermore, a YAG based (or TiAl₂O₃ based system if available at that time) KHz repetition rate laser, tunable in the visible and IR shall be needed. A multichannel photon detection system shall complete the equipment needed for this type of experiment.

C. Instrumentation of more general use

A low temperature (liquid He) cryostat with optical interface and IR probe lasers of high stability and reasonably broad tunability shall be needed.

D. Estimated total cost

The cost of the instrumentation listed above is estimated to be about \$1.5 million.

F. COMBUSTION DIAGNOSTICS

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The working group on Combustion Diagnostics considered three aspects of the proposed Combustion Dynamics Facility:

1. The scientific value of the CDF to combustion diagnostics
2. Facilities that are particularly important to combustion diagnostics
3. The users program

THE SCIENTIFIC VALUE OF THE CDF TO COMBUSTION DIAGNOSTICS

A. Chemical Dynamics Studies

The knowledge of the mechanisms and dynamics of elementary reactions, the elucidations of primary photodissociation pathways, and the identification of reaction intermediates constitute the essential scientific basis for the further development of combustion diagnostics. The experiments performed with the ALS and IRFEL facilities at LBL and the femtosecond laser facility at SNL and improved computational capability of the CCCS will greatly increase this crucial scientific base.

B. Spectroscopy of Reaction Intermediates

Perhaps the most important limitation on the present application of laser based methods for the monitoring and detection of combustion species is the lack of spectroscopic information on radical reaction intermediates. The wide tunability and high intensity of the ALS and IRFEL are attractive for measurements of ionization potentials, vibrational frequencies and molecular structure in several varieties of experiments. IR pump and VUV probe experiments are particularly attractive. The available resolution of the IRFEL of about 3 cm^{-1} can be useful for survey spectra designed to take full advantage of the wide tunability of this device. Efforts should be devoted to the use of external optical techniques for the narrowing of the effective bandwidth of the IRFEL source to $<0.1\text{ cm}^{-1}$ to permit rotationally resolved vibrational spectroscopy. The use of the ALS with advanced IR lasers of narrow bandwidth meets the need for a narrow bandwidth source for wavelengths below 10 microns.

Because many radicals of importance do not fluoresce strongly, the sensitive technique of resonance-enhanced multiphoton ionization (REMPI) spectroscopy is an important diagnostic method for the *in situ* measurement of species profiles in flames. Application of this technique is severely limited by a lack of spectroscopic information on Rydberg states of these transient species. Experiments the ALS and IRFEL in which VUV pumping is combined with either IR or visible probing may provide a rapid means for low resolution detection of these high lying molecular states. Increased emphasis should be placed on *ab initio* calculations of Rydberg states of combustion radicals to meet present diagnostic needs.

C. Studies of Chemical Kinetics and Energy Transfer

The multiple beam Nd:YAG dye laser system proposed for the Sandia CRF is an important new innovation of considerable significance for kinetic rate constant measurements and studies of reaction mechanisms. Laser based kinetic rate measurements performed in recent years and Sandia have had an important influence on the laser diagnostics and combustion modeling communities. Leadership at Sandia in the development of this valuable new users facility will permit new kinetic measurements to be performed on reaction systems of importance in the combustion of toxic materials.

D. The diagnostics of Turbulent Reacting Flows

The multiple beam Nd:YAG dye laser system will provide a unique and critically important capability for measurements of turbulent combustion. The ability to make multiple species measurements with temporal and spatial correlations and the use of 2-D and 3-D imaging methods will provide fundamental new data on complex interactions in turbulent reacting flows. The accomplishments to date in this field both at the Turbulent Diffusion Flame Facility at Sandia and at other laboratories have

validated this new experimental approach. The Turbulent Diffusion Flame Facility coupled with the multiple beam Nd:YAG dye laser facility will be a unique and extremely valuable asset to the nation and the international combustion community.

E. Soot and Smoke Diagnostics

Thought should be given to a new facility designed to make use of the unique turnability and high intensities of the ALS/IRFEL lasers. Data on soot particles have been obtained almost exclusively using visible radiation. Opportunities for new information on particles exist at both long and short wavelengths, which would help characterize the growth and oxidation of soot particles, their morphology and their radiation properties. At long wavelengths ($5\text{ }\mu\text{m}$) the Rayleigh assumption (diameter $\ll \lambda$) is universally valid for soot within flames. At these wavelengths less scattering occurs and more direct extinction measurements can be made of the soot volume fraction (often the most important soot parameter one wishes to know). At short wavelengths ($<200\text{nm}$) the growth of primary soot particles ($10\text{-}40\text{ }\mu\text{m}$) may be studied in the Mie scattering regime. Detailed angular scattering measurements may be able to separate the effects of primary particles from flame-generated agglomerates.

FACILITIES OF IMPORTANCE FOR DIAGNOSTICS DEVELOPMENT

A. The Center for Computational Combustion Science (CCCS) and the CRF Laboratory Facilities

The CCCS computational capabilities will couple the experimental capabilities of the CRF and the CDRL with theory to create new predictive combustion models. More extensive modeling capabilities are needed in the design and monitoring of engines, coal combustors, furnaces, boilers and municipal and hazardous waste incinerators. New approaches to the combustion of toxic materials employing very combustion pressures will require new modeling efforts facilitated by the CCCS.

B. Multiple Beam Nd:YAG Dye Laser and Turbulent Diffusion Flame Facility

This innovative new facility with capabilities for multiple species diagnostics and for the 2-D and 3-D imaging of turbulent flames with temporal and spatial correlations will require a major investment in new experimental equipment. Several new 2-D array cameras and image analysis equipment is needed. A multiple user laboratory access to the laser facility must be provided so that several different experimental stations can be used. The technology of the imaging field is growing rapidly and thus an emphasis must be placed on continuing upgrades of experimental capabilities.

C. Toxics Combustion Facility

It is proposed that a major new laboratory users facility be constructed at the CRF to permit international participation of researchers in studies of incineration of toxic materials. The need for diagnostic research on toxic and hazardous substances is increasing as the potential problems associated with combustion generated pollutants are being re-examined. For many toxic substances there are no existing methods available for their real time measurement. In addition, the products and intermediates of most reactions of species such as chlorinated hydrocarbons are not known and the majority of the rate data needed are not available from experimental studies. This condition limits modeling efforts to a fitting of existing data rather than providing reliable predictions of combustion performance and complicates the implementation surrogate monitoring.

Diagnostic research at the CDF could provide a wealth of information on the spectroscopy of numerous molecules and radicals that have not been studied extensively, either under well controlled conditions, such as in molecular beams, or at the high temperature pressure conditions associated with normal combustion. Identification of reaction pathways is also important, as potential means of controlling undesirable product formation will be revealed. Rate data will reduce uncertainties in the kinetic models, greatly increasing their utility.

A dedicated laboratory facility for combustion research involving toxics is desirable. This facility would have the capability to handle and store toxic and carcinogenic compounds, with no danger to researchers, including visiting scientists and their students, who may have little or no formal training in the safe handling of dangerous materials.

This important new users facility should be equipped with a full range of optical diagnostics designed to monitor both major species and reactive intermediates. Molecular beam sampling and FTIR facilities should be available for research in this facility.

D. Improved Resolution for the IRFEL Source

The utility of the IRFEL as a bright, tunable laser source will be greatly increased if means can be found to overcome the limitations of a relatively large bandwidth and frequency jitter. The principal advantage of the IRFEL for absorption spectroscopy is its wavelength flexibility. The infrared spectrum is relatively congested in hydrocarbon flames. Thus a central problem in IR combustion diagnostics is the identification of transitions that are relatively free from interferences from other species but are sufficiently strong to provide sensitive detection.

Typical Doppler widths for flame species at 2000 K are 0.25 cm^{-1} . Thus the bandwidth and frequency jitter of the proposed IRFEL ($3 \text{ cm}^{-1} + \text{jitter}$) of the proposed IRFEL are not suitable for flame diagnostics of interesting radical species such as ethynyl (C_2H) and vinyl (C_2H_3) radicals. Survey scans may not be able to provide useful spectral information and may be plagued by interferences (H_2O , CO_2 , etc.) in flame environments. A bandwidth of $<0.1 \text{ cm}^{-1}$ and a center frequency jitter of $<0.1 \text{ cm}^{-1}$ would be desirable for useful spectroscopic experiments. The use of external interferometric and Fourier transform techniques for bandwidth narrowing should be explored as a way to circumvent the present IRFEL source limitations.

PROPOSED MODIFICATIONS TO THE USERS PROGRAM

The working group considered modifications to the users program to facilitate combustion diagnostics.

A. Proposed Improvements to the Sandia Users Program

The Combustion Research Facility has successfully conducted an excellent visiting scientists program for a number of years which serves as a model for other facilities including the CDRL. There are, nevertheless, improvements that could significantly assist research participation in important new areas of combustion science including the incineration of toxic materials, high pressure combustion, coal combustion, utilization of alternative fuels and fundamental studies of turbulent reacting flows. The new multiple-beam Nd:YAG dye laser and femtosecond laser facilities present an opportunity to greatly improve and expand the CRF visitors program which promises significant further productivity for the CRF.

Additional Equipment is Needed

The visitors program has reached a stage of successful maturity that warrants a re-examination of the use of major laboratory equipment. Equipment specifically allocated to the users program would add flexibility to collaborative research. A Fourier transform infrared spectrometer, a dedicated flame sampling mass spectrometer apparatus designed for transient radical monitoring and tunable diode lasers for IR spectroscopy are examples of such equipment that could be dedicated primarily to the users program. The technical assistance needed for the operation of this equipment would require only a modest expansion of the already excellent technical assistance program at the CRF.

Toxics Combustion Facility for Visiting Scientists

Major obstacles encountered by potential researchers interested in contributing to solutions to the national problem of hazardous waste disposal are the difficulties in acquiring and managing experimental facilities capable of handling the combustion of toxic and corrosive materials. Questions of safety and cost generally rule out effective

experimental research programs at universities. The CRF could gain immediate international visibility if it were to successfully initiate a users facility dedicated to experimental studies of toxic waste incineration equipped with a full range of laser-based diagnostic techniques. Successful studies of the chemical dynamics and kinetics of elementary reactions in the combustion of toxic materials and the development of predictive models ought to be primary goals of the proposed Combustion Dynamics Facility at LBL and SNL. A highly visible dedicated toxics combustion facility at the CRF would validate these concerns.

Unrestricted Access

The present visitors program at the CRF is needlessly hampered by security regulations that restrict the independent participation of visiting scientists. The present arrangements are inefficient and present inordinate demands on the time of the permanent CRF staff. Part of the users program might consist of independent research without direct participation of the in-house CRF scientists. Thought should also be given to the means by which nonacademic researchers might gain financial assistance while engaged in collaborative research.

Standardized Test Bed Facilities

Burner facilities with well-documented characteristics would be very useful for the development of new diagnostic methods. If, for example, major species profiles and temperatures were documented for a given apparatus operating under specified controlled conditions, much needless repetition and error would be eliminated from future studies with that apparatus.

Proof of Principle Experiments

One of the most valuable aspects of a users facility is the provision for short duration experiments designed to try out new concepts. Consideration should be given to the facilities and technical assistance needed for such proof of principle experiments.

Improved Publicity

Better publicity concerning the Sandia users program should be directed toward potential users. This should include publicity concerning the implementation of modeling codes developed at Sandia for user-based applications.

B. Coupling Between the CDRL and the CRF

A crucial issue in the success of the proposed CDF will be the interactions between those engaged in applications - oriented research and those performing fundamental studies of chemical dynamics. The study group considered some possible steps to facilitate such interactions.

Personnel Interchange

Interactions between LBL and SNL ought to be streamlined to permit students, postdocs and researchers to move back and forth between the two organizations. A sabbatical leave program for senior researchers ought to be considered.

Scientific Conferences

An annual joint CDRL-CRF scientific workshop patterned after the very successful annual DOE contractors meeting conducted by Dr. Laufer of the Chemical Sciences program ought to be organized. A well publicized less formal series of weekly seminars at both the CDRL and CRF is also quite important.

The Role of the CCCS

The Center for Computational Combustion Science is a natural conduit for interactions between *ab initio* theorists and those engaged in the development of advanced predictive combustion models.

Applications Requirements as Input for Scientific Studies

Applications in toxics combustion, NO_x reduction, metals combustion, soot formation, high pressure combustion, energetic materials, alternative fuels, coal combustion, engine development, etc., must inform the chemical dynamics studies. Diagnostics development and kinetic modeling must also inform the chemical dynamics studies.

G. IRFEL TECHNOLOGY

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The IRFEL working group discussed two different classes of issues in the design of the IRFEL facility—accelerator issues and optics issues. We also spent a brief time discussing the FEL undulator. We will summarize these issues below.

ACCELERATOR ISSUES

The accelerator is similar to the accelerator which operated for several years at Los Alamos National Labs. The required longitudinal brightness is similar to that achieved at Los Alamos for similar pulse charge. The transverse emittance specified in the design is a factor of two better than the Los Alamos system achieved at the same pulse charge. The Los Alamos system was designed for higher charge per pulse however and better performance is expected from a system optimized for 1 nC operation. The design seems to have incorporated design changes which reflect problems encountered in the Los Alamos machine. We were concerned with several issues addressing this area.

A. Stability

The stability of the Los Alamos machine was not adequate to meet the specifications for the device needed here. Careful attention needs to be paid to reducing accelerator instabilities. It was noted that the machine would probably not operate stably at 50 Hz. The machine should be locked to the line frequency of 60 Hz. This has been necessary even in the Stanford superconducting accelerator which has the capability of stable operation at any frequency. Users at Stanford have tried to operate at a frequency which was not locked to the line but finally chose to operate at a subharmonic of 60 Hz in order to optimize the machine stability. It should be noted that the machine will cause significant noise on the line voltage and steps must be taken to separate the ac supplies for the users and the accelerator. In principle, one of them could be isolated to the point of operating at a different frequency from the line. We should stress that the accelerator and all of its ancillary supplies, even the lights in the vault, must be locked to the same frequency whatever that frequency may be.

The system will use both feedback and feedforward to stabilize the phase and gradient in the accelerator structures. Secondary control loops stabilize the beam position, accelerator temperature, and mirror alignment. A final loop corrects the accelerator gradient to keep the optical spectrum constant. This can probably only be done on a slow time scale, but feedforward techniques might be used to get rid of any fast noise if it is repeatable. This loop demonstrates a philosophy which the working group decided was very effective—one's best diagnostic of the accelerator behavior is the laser output. This philosophy also leads one to consider using the laser beam position to correct the electron beam position in the undulator. Other feedback loops which would be useful are a measurement of the cavity ringdown to monitor the optical cavity alignment, and a loop to maximize the spectral intensity of the macropulse using the cavity length.

One complication in using the wavelength to measure the energy is that several factors affect the laser wavelength. Redundant measurements of the energy are therefore needed to keep it from drifting too far from the set point. Since the highest dispersion point in the electron beamline is after the laser, the electron momentum spectrum cannot be measured accurately when the laser is lasing. One can measure the beam energy before the laser turns on but this is not useful since the feedback loops have not come into regulation yet. One must, therefore, kick out the first part of the electron beam in order to let the electron beam settle down. It was not decided whether a magnetic or electrostatic deflector would be more effective in accomplishing this.

The overall feasibility of the feedback system looks good. The loop gains for the full beam energy look quite reasonable (the bandwidth indicated in the original report was actually larger than necessary by a factor of two due to the assumed length of the optical cavity). The loop gains necessary at the lowest energy need to be calculated. Furthermore the overall architecture of the feedback/feedforward system needs to be laid out. The time response for each loop and possible interactions between loops needs to be worked out.

B. Subharmonic bunchers

The lower current in this system should reduce problems encountered in the Los Alamos system. Two potential problems in these devices are multipactoring and higher order beam breakup. The cavity designs need to be optimized to minimize these problems. Computer codes are available to study these problems and find ways to eliminate them. They can be checked for reliability by using the ALS injector as a testbed.

C. Wakefields

No calculations were done in the proposal to find the effect of wakefields on the emittance and energy spread of the beam delivered to the laser. This is especially important at the low energy end of the accelerator where wakefields are quite important. Techniques have been developed to minimize emittance and energy spread growth due to wakefields. These should be used to design the vacuum chamber used to transport the beam to the FEL. This area is rather critical since the longitudinal brightness is very important to the FEL gain. Specifically, the FEL gain is inversely proportional to the longitudinal brightness for this design. If the energy spread grows by a factor of two, the gain will decrease by a factor of two. The transverse emittance is not nearly as critical. A factor of two increase in the emittance only drops the gain by 20%.

D. Energy tuning

It may be desirable to scan the electron beam energy by a couple of percent either over a period of minutes or even in a single macropulse. This has been done at both Los Alamos and Stanford. The laser can easily slew one linewidth per small signal gain e-folding time in the long wavelength direction. The electron beamline should be looked at to see if it has adequate energy acceptance to accomplish this. Sextapoles might be needed to accomplish this.

E. Diagnostics

As mentioned above, the most sensitive diagnostic for the accelerator is the laser. Other diagnostics are nevertheless necessary to set up the beam to the point where stable lasing can be achieved. The most important parameters to know are the current and energy of the electron beam on both fast (psec) and slow (μ sec.) timescales, and the beam position in the undulator. Streak cameras can be used to measure the current vs. time on both long and short timescales. Development of these cameras has been quite rapid and it is expected that they should be relatively inexpensive and easy to use by the time this system comes on line. They do have problems with radiation, so a

telescopic imaging system should be developed which can image the light from a Cerenkov screen onto the slits of the camera, which would be placed well away from the beam. The streak camera is especially useful because it can be used at several locations in the beamline to check out the performance of different segments of the accelerator. If the screen is placed at a point of high dispersion the streak camera can be used to measure the momentum spectrum as function of time. Newer synchroscan cameras can have two sets of orthogonal plates which drive the beam at different rates to get micropulse and macropulse information in a single sweep.

An rf deflection scheme could be used at fairly high cost to measure the current vs. time at one location. The current proposal calls for one of these after the buncher. This system does have the advantage over a streak camera of being able to measure the phase jitter quite accurately. It is not clear whether synchroscan streak cameras can do this with as much sensitivity at this time. The need for an rf deflection system cannot be justified on these grounds however since phase jitter can be measured using an inline low Q resonant cavity.

Beam position monitors on this system need to have a sensitivity of 50 μm and an accuracy of a couple hundred μm . This seems achievable with present stripline technology if some signal averaging is done. Many of these should be used. There is probably not room for these in the undulator vacuum chamber so screens will have to be used here. Beam position monitors before and after the undulator must be sufficiently densely placed so that the entrance trajectory can be reliably set up. Cerenkov radiation screens appear to be the most robust and linear. There should be at least 5 in the wiggler vacuum chamber in order to set up the vertical orbit of the beam (the beam can be strongly focussed in the vertical dimension, leading to an oscillation in height). Some of the cameras for the screens should be equipped with gated image intensifiers to look at one part of the macropulse at a time.

Several low cost diagnostics such as wall current monitors, toroids, and a pepper pot to measure low energy emittance should be used. One toroid after the accelerator and one at the beam dump need to be dedicated to a transmission measurement which can be interlocked to the gun when the system is run at full beam power.

Radiation monitors in the vault monitor the amount of lost beam instead of the amount of transmitted beam and are therefore quite useful in diagnosing slight misalignments or beam scraping.

A very useful diagnostic which is not usually thought of is the experimenter's signal. When this signal is monitored, the operator can be alerted to small changes in the accelerator status which he or she would not otherwise notice.

F. Multiplexing

In principle, one could serve several users at once if the macropulses were multiplexed to the experiments. This would require them to operate at the same wavelength and time structure. In fact, it is possible to operate at two wavelengths which differ by a few percent and have a different time structure. It would be nice if the accelerator were capable of operating in this interlaced mode.

G. General notes

The performance of the system should be calculated using PARMELA for several different energies to be used in operation. These results should then be used to model the gain and output power of the system. It should be noted that the gains shown in the proposal to date reflect incorrect assumptions about the energy spread. As realistic values as possible should be used for the prediction of low energy gain. The possibility of operating with 2 nC at low energy has been suggested. This will probably increase the energy spread and emittance and reduce the beam stability, but can be looked at as a way to increase beam power with some decrease in performance. Again, the growth in longitudinal emittance is the big problem here.

OPTICAL SYSTEMS

In contrast to the accelerator, the optical system is a large jump from any existing system. There are therefore some uncertainties in predicting the performance levels. Although the Los Alamos System has operated in the wavelength range from 8 to 45 μm , it was not operated as a user facility. The output coupling efficiency and mode quality in this range were therefore not an issue. The wavelength range from 15 to 50 μm is one of the most difficult wavelength ranges in the electromagnetic spectrum to operate. The choice of optical materials is one important issue. The optical transport design is also more difficult than in the visible because of the increased diffraction. Optical design is made still more difficult by the desire to scan over the entire 3 to 50 μm range in very little time. Ideally, one would want to keep the same optics for the entire range. Almost as good would be a quick switch of optics which would take at most a few minutes. Actually having a vacuum break and changing a mirror takes several hours even if the system is designed to make changing mirrors easy. Many design issues cannot be addressed adequately at this time due to the lack of a technical database on high power optics in this wavelength range.

A. Output Coupling

This seems to be the biggest problem facing this entire device. The demands on the output coupling are severe. The optics must operate throughout the wavelength range without significant absorption. They must withstand fluences of 50 J/cm^2 for a $100 \mu\text{sec}$. macropulse. They must be compatible with the high vacuum of the optical cavity and resist the high levels of ionizing radiation in the vault. The outcoupling efficiency must be reasonably high and the power should be outcoupled without seriously disturbing the excellent mode quality inherent in the FEL. The conclusion of the working group was that a solution to this problem has not been found.

Several possible output coupling were looked at. The results are summarized in Table 1.

Table 1 **Possible output coupling alternatives**

Method	Advantages	Disadvantages
Hole coupling	<ul style="list-style-type: none"> • No dielectrics needed • Could use extra output coupling as monitor • Demonstrated technique over the entire λ range 	<ul style="list-style-type: none"> • Output is not TEM_{00} • Output coupling is dependent on wavelength • Output coupling efficiency is modest • Optical transport is difficult
Brewster plate with single surface AR coating	<ul style="list-style-type: none"> • TEM_{00} output • Proven technology • Easy from 3 to $15 \mu\text{m}$ 	<ul style="list-style-type: none"> • Must change plates to shift wavelength ranges • Coatings and substrates difficult to find at $\lambda > 15 \mu\text{m}$ • Causes cavity length to depend on wavelength • Two pulses out-coupled
Metal grid on mirror	<ul style="list-style-type: none"> • TEM_{00} • Single output pulse • Excellent out-coupling efficiency 	<ul style="list-style-type: none"> • Possible damage problems • Need transmissive substrate (does not have to withstand full intracavity power)

The use of dielectric quarter wave stack mirrors was judged as too unwieldy for such a broad tuning range. It also is a problem at long wavelength due to the lack of suitable materials. Hole output coupling has been studied at LBL and was used in the Los Alamos device. A variation on this technique using a small suspended mirror was used at the University of California at Santa Barbara. Several groups are presently considering the use of this technique for this wavelength range. An interesting addition in the LBL design is the presence of an annulus of variable size to confine the optical mode. This preserves the optical mode shape as the wavelength changes and has the advantage of being useable as a monitor of the laser power without disturbing the output beam. A variation on hole outcoupling is the unstable resonator. This has all the problems of the hole outcoupling and a few others. Unless some new scheme is developed which solves some of these problems, it does not seem to be an attractive approach.

Brewster plate output coupling has been used at Stanford. This technique results in four output beams. If the intracavity fluence is low, one can add an anti-reflection coating to one side of the plate to reduce the outcoupled power to two beams. This makes the plates have a narrower bandwidth than an uncoated plate but, since they are flat, they can easily be switched in and out without changing the cavity alignment. Free-standing diamond pellicles could be used for the long wavelength end of the range but are quite new and untested.

One possible technique which was discussed is to use a transparent substrate with a metal coating on it for one of the cavity mirrors. The coating would have submicron width lines cut through to the substrate. The spacing of the lines would be smaller than the smallest wavelength used ($3\text{ }\mu\text{m}$). Present lithographic techniques allow $0.5\text{ }\mu\text{m}$ linewidths to be achieved which would allow one to build a mirror with 16% output coupling. It is not known whether such a mirror could be built at this time or whether it could withstand the peak fluency or the average power in this laser. It should be noted that the inverse of this pattern could be used as a pellicle on a Brewster plate. This would be quite useful in the long wavelength range where an AR coated Brewster plate would be difficult to build.

In conclusion, much work needs to be done to find a good solution to this very difficult problem. Both experimental work and research needs to be carried out. Close attention should be paid to ongoing efforts at other projects which intend to operate in this wavelength range.

B. Optical diagnostics

The technique of frequency conversion to the visible via metal vapor has been proposed to convert the entire spectral range of 3 to $50\text{ }\mu\text{m}$ into the visible. This would allow the use of readily available optical diagnostics which exist in the visible such as streak cameras, spectrometers, optical multichannel analyzers, Pockel cells, and reticon arrays. Pyroelectric detectors, a calorimetric powermeter, thermal plates (for beam position

monitoring), pyroelectric quadrant detectors, and fast quantum detectors will also be needed. An autocorrelator should be available for cross checking the streak camera measurement of the upconverted microbunches. Characterization of the spontaneous radiation is quite difficult and does not give much information about the gain of the laser. It is useful, however, to have a detector which is sufficiently sensitive to measure the spontaneous radiation through a monochromator with reasonable signal to noise (e.g., a helium cooled bolometer). This need only be done in the short wavelength end of the range. Once the system is commissioned, pyroelectric detectors can be used to study the system in the long wavelength range. If the harmonic upconversion idea does not work out, it will be necessary to purchase several monochromators and pyroelectric arrays to act as optical multichannel analyzers for several ranges in the infrared. Having a continuous monitor of the optical spectrum during tuneup and station keeping will be essential. It will form part of the feedback loops which control the electron beam energy and cavity length.

One extremely important diagnostic to the user is the availability at any time of a collinear alignment laser. Methods should be developed which allow this beam to be coaligned with the FEL beam.

Several miscellaneous items will be needed. An optical gate would be useful if possible. This can be done in the 3 to 15 μm range by using a semiconductor switch as was demonstrated at the University of California at Santa Barbara. Polarizers using stacks of transparent material can be used in the short wavelength range as optical attenuators or as polarization rotators. Transient digitizers of moderate speed will be necessary to capture the fast signals and relay them to the computer. Finally, the cavity length must be monitored using some absolute measurement device such as an interferometer.

C. Optical Transport

Although a cryopumped evacuated optical beamline is workable in principle, it is not desirable in practice. A helium filled system is easier to operate and cheaper to build. Thermal blooming, scatter, and absorption are not important in this gas.

D. Tuning range

The present design calls for a movable vacuum chamber in the wiggler which would allow the entire range of wavelengths to be covered with three different electron beam energies. If this idea does not work, the system will have to be operated at four different energies instead. This does not seem to be such a large loss if the control system is designed correctly.

E. Resonator Stability

The stability tolerance for the mirrors is $\pm 10 \mu\text{Rad}$. This is easily achieved in present optical cavities. Since no water cooling is required on the mirrors, no vibration from any mirror cooling system is expected to strongly effect operation.

F. Harmonics

Wavelengths shorter than $3 \mu\text{m}$ can be easily achieved using harmonic generation in non-linear crystals. The conversion efficiency already demonstrated has been 10% to the fourth harmonic and 50% to the second harmonic. Conversion efficiency of a narrowband pulse with good spatial mode quality can in principle be as high as 50% to the fourth harmonic. This capability should be available to the users.

The laser also produces copious amount of coherent spontaneous radiation at the harmonics. This may be as high as 1% at the second harmonic. Filters will have to be developed which can be used to cut off the harmonics.

G. Multiplexing

This was mentioned previously in conjunction with the electron beam controls. It would be useful to multiplex the beam to two or more users.

H. Efficiency enhancement

In principle, one could taper the undulator or use some other technique to enhance the efficiency of the laser. Unfortunately, this would lower the gain. The reduced gain would not allow one to operate with narrow bandwidth at the long wavelength end of the wavelength range. Since the users are more interested in spectral brightness than in pulse energy, efficiency enhancement is not recommended.

I. Conclusions

In general, the accelerator design seems sound. Some things need to be looked at which might degrade performance below specifications. The most serious concern is that the longitudinal brightness might not meet specifications when wakefield effects and single bunch beamloading is added to the simulations.

The optical design needs quite a bit more work before one could say whether it will satisfy the strict demands of a user facility. Close attention should be paid to efforts at other labs to operate in this wavelength ranges.

SUMMARY OF RECOMMENDATIONS

1. Operate the machine at some subharmonic of 60 Hz and lock the machine to the line.
2. Use kicker to eliminate the initial transient in the electron beam. This idea needs further work but it is desirable to implement.
3. Use the laser output to stabilize the final energy of the electron beam and the beam position and cavity length.
4. Recalculate the behavior of the accelerator using PARMELA for the lower energy cases.
5. Recalculate the loop gain for the worst case situation of high current at low energy.
6. Define the loop architecture and the timescales for the various feedback and feedforward loops.
7. Investigate the design of the subharmonic bunchers with regards to beam breakup and multipactoring. Use the ALS injector to benchmark the predictions.
8. Design the beamline with wakefield effects in mind. Try to calculate the growth in both transverse and longitudinal emittance from a reasonable design.
9. Look into the possibility of varying the energy of the electron beam on a fast time scale. What is the energy window of the transport system?
10. Provide the electron beam diagnostics listed in this report. We do not recommend an RF deflection system at this time. A combination of a streak camera and a low Q resonant cavity on the system will do. Implement a design philosophy which eases the task of an experimenter providing a signal to the operator.
11. Study the possibility of stretching microbunches and reducing the energy spread. Does this increase or decrease the maximum spectral brightness?
12. Look into beam multiplexing.
13. Study any outcoupling scheme which looks like it may work. A great deal of work needs to be done to come up with a working solution here. Some new technologies such as partially transparent metal mirrors and diamond film pellicles need to be studied.

14. Provide the optical diagnostics listed in this report. Verify that the upconversion process will work in the wavelength range of the laser. Some development work may be necessary for some of the pyroelectric detectors in order to improve their speed or sensitivity.
15. Use a helium filled transport line unless some fundamental objection to it is found.
16. Work out the details of an interchangeable vacuum chamber for the undulator. Is it really feasible?
17. Look into providing harmonic rejection filters for the entire range (at least 4 will be required) and crystals for harmonic conversion into the 0.75 to 3 μm wavelength range.
18. Study the possibility of multiplexing the optical beamline.

H. ALS BEAMLINE TECHNOLOGY

Group Members

Dave Attwood
Malcolm Howells
Masato Koike
Volker Saile
John West (Chairperson)

Dave Ederer
Brian Kincaid
Jay Marx
Jim Underwood
Mike White (Liaison)

BEAMLINE DESIGN

The designs for the two normal incidence beamlines described in the CDF conceptual design report were examined in detail, and it was considered that they would meet the requirements for a resolving power of 50,000 in the photon energy range 5 - 25eV. It was not known if these designs had been raytraced and this was considered to be an essential next step. There was marked scepticism over the proposal to scan the undulator gap in synchronism with the monochromator and it was decided that it would be acceptable, at first, to make wavelength scans over a small wavelength region within the width of the undulator harmonic until confidence in the synchronous mode was built up. This restriction would not be particularly serious if the monochromator was being run using its high resolving power and a commensurate scanning mesh.

The horizontal acceptance of the bending magnet design was discussed in some detail. It was proposed that the optical system would need to move closer to the ring to gain full advantage of the 10 milliradians available, to avoid the need for a very large first optical component. In its turn this would mean moving part of the CDF into the ALS experimental area. Thus, some redesign of this beamline would be necessary, should it be decided to go ahead with a second normal incidence facility.

WAVELENGTH COVERAGE

Both this panel and that discussing photoelectron-photoion processes were concerned that the choice of wavelength range was too restricted. The undulator beamline was considered to have the higher priority, because its performance would exceed, by at least two orders of magnitude, the intensity at very high resolution available anywhere else. However, the bending magnet beamline would provide a performance merely equal to that available currently elsewhere, so serious thought should be given to modifying this part of the proposal. A medium energy spherical grating monochromator was suggested as a possibility, to extend the photon energy range up to 100eV, and soft X-ray capability was also mentioned.

This panel suggested that this option be left open for the time being; if survey-type broad wavelength scans are seen to be an important part of the CDF scientific program, then indeed the normal incidence bending magnet beamline would fulfil this purpose. It was pointed out that a third dipole magnet is available to the facility, and it would be wise to reserve this for use by the CDF though clearly funds beyond those presently envisaged would be required to instrument it.

ORDER SORTING

This topic was discussed at length and it rapidly became apparent that light of high spectral purity was essential for the success of much of the science being proposed. The ambitious target, to provide radiation where the contamination from higher orders and scattered light was less than one part of 10^5 was set. The two normal incidence reflections in the beam lines proposed, go some way to providing this, and LiF windows will provide freedom from higher orders for energies lower than 10eV. The major problem occurs in the region between 10 and 15eV, and for this a rare gas filled order sorting system was discussed. It was decided that this would have to be installed after the exit slit of the monochromator, where there would be conflict between the small apertures required for differential pumping the larger ones to allow the diverging beam from the monochromator to pass through: the use of capillary arrays was suggested as a solution to this problem. The scheme, though feasible, was going to be hard to implement and further thought on the detailed design was necessary, particularly since this seemed to be the only solution available. The possibility of using "laminar" profile gratings to suppress even orders was discussed but experience elsewhere had shown that these were not as efficient as blazed gratings and they also varied somewhat in their ability to suppress second order. Predispersing optics were mentioned and have indeed proved to be a good way to remove scattered light, but would be little help unless used in different orders, with consequent inefficiency. Should a high energy photon beam be implemented, the situation would be eased since

selective reflection techniques could be used, but no simple solution was suggested for the 10-15eV photon energy range.

BEAM LINE ALIGNMENT

Conventionally, initial alignment of beamline optical components is done using white light, with monochromators set on zero order. With undulators this option will not usually be available, so other methods must be found to detect the VUV photons; even the beamline laser system used on some present day facilities may not be sufficiently accurate. Various options, semiconductor diodes, scanning wires, fluorescent screens were discussed, but the beamline must now include this as an integral part of the design since it will be difficult to add on as an "afterthought." With a high brilliance source, as the ALS will be, precision alignment of the monochromator pre- and post-optics will be of paramount importance. Detectors will need to be placed near all the foci of the optical system; such detectors will have to be position sensitive with a precision better than the size of the focused image at that point, and also be UHV compatible. Also, they should be placed behind the exit and entrance slits of monochromators, where perhaps the position sensitivity in one direction can be relaxed since their main function will be to measure intensity. With the beamline in normal operation most of these detectors will have to be moved out of the way, with the requirement therefore for kinematic translation mechanisms. Considerable thought and care will have to be applied to this aspect of the beamline engineering design.

USE OF TOXIC AND CORROSIVE GASES

This was an issue discussed by several panels; the main concern of this panel was to keep the beamline optics clean and experience on other facilities has shown that hydrocarbons and corrosive gases must be kept below a partial pressure of 10^{-13} mbar to protect the optics properly. Even at this level, where optical light guides or long differential pumping apertures are in use contaminants tend to be "channelled" unavoidably, towards the optics. The beam lines proposed for the CDF make use of post focusing optics, which will help if the final component is cheap and readily replaceable. Also the issue of the use of diffusion pumps was raised in the general meeting. Certainly these pumps have the performance required, but the consequences of pump failure or malfunction are very severe, particularly since most precision optical components cannot be baked to high temperature to remove contamination. The continuing development of high speed turbomolecular pumps should help to resolve this issue.

The use of communal multipurpose experimental chambers did not seem viable where corrosive gases were to be used: in many cases it may not even be practical to reduce contamination in the chamber to a low enough level for the next experiment to be unaffected. It may well be that separate experimental chambers with their own set of detectors will have to be used for this kind of work. The emphasis must remain on keeping the beamline clean to a very high standard and there will be some dependence on the cooperation of the individual user.

ALS RUNNING CONDITIONS

The panel could only make general comments on this topic; there was a requirement for timing experiments and 8-bunch running of the source seemed a good compromise between intensity and timing interval between pulses. Beam lifetime was also an issue; experience on other facilities has shown that long lifetimes, in excess of twenty hours, have been a great asset to the experimental program. Accepting that this does not appear to be feasible on the ALS, it was suggested that with a modest sacrifice in the brilliance of the source, lifetimes longer than six hours would be valuable for medium resolution studies. For the high resolution work, however, the loss in intensity resulting from this would not be acceptable.

I. THEORY AND COMPUTATIONAL REQUIREMENTS

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Rod Bartlett
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M. Koszykowski
Horia Metiu
Bill Miller
Moshe Shapiro
Al Wagner (Chairperson)

The discussion of our committee was in the context of the existing proposal, which is largely experimental. We tried to frame our discussion within the limits of this proposal. We did not focus on what form a major theoretical effort would take to address problems in chemical dynamics and combustion, if we started from scratch.

The purpose of the theory effort of this proposal generated considerable discussion which is condensed as follows.

One part of the group is interested in primarily collaborative interactions with the experimental program. Since the experimental program is concerned with chemical dynamics, most of these people are chemical dynamicists and they look forward to a close collaboration with many of the excellent experimental programs that were discussed earlier in the day.

Another part of the group sees the theory effort as a unique opportunity to bring together the modelers and the molecular levels scientists, both theorists and experimentalists, to produce predictive simulations of real world combustion problems. These people are actually thinking about modifying designs of practical devices by full integration from the fundamentals at the chemical dynamics level, all the way through the kinetics, and into modeling the simulation of actual devices. They see the value of the theoretical effort not just exclusively helping, or collaborating, with the experimental program but, if necessary, providing calculated information directly that would become

important input to predictive simulation. This part of the group favors a more combustion driven simulation aspect to the theory.

There is a minority part of the group who considered that the CDF is not accurately named, that in truth this proposal is a chemical dynamics proposal, not a combustion dynamics proposal, and that by using the word combustion, we are deluding less informed policy makers into thinking they are investing large sums of money in combustion work when they are really investing in chemical dynamics work. From this point of view, this part of the group looks towards the theory as being an effort to reach out to the full combustion community by actually demonstrating that the integration of fundamental information from theory and experiment, all the way through predictive simulation, can have an impact on the real world of combustion items.

The group, as a whole, made a list of the important opportunities for the theory portion of the proposed facility. This list was divided into two categories: the molecular level and modeling and simulation level.

MOLECULAR LEVEL

The calculation of electronically excited surfaces and non-adiabatic coupling elements: There are many calculations these days done on ground state surfaces. Electronically excited state surfaces, especially those of the same symmetry as lower states, are difficult to do. Non-adiabatic coupling elements are just coming into their own, and labelling them as coupling elements is probably a misnomer; they are really coupling surfaces with as many dimensions as the surface.

Calculation of electronically ground state surfaces for aromatics, complicated radicals, clusters, gas-solid interactions: Theoretical calculations in these areas are often not at a level of accuracy to be predictive, and competitive, with experimental studies. Work in this area is more than just increasing the number of CPUs that you throw at the problem, although this is part of it. Involved also is the development of new techniques and methods.

Calculation of an harmonic spectra of large molecules: The larger the molecules the more work that needs to be done on the accurate solution to the nuclear Schödinger wavefunction, to produce spectroscopically reliable and harmonic spectra, which can be of assistance in the experimental program. Once the energy increases beyond the lower levels, vibrational-rotational motion will manifest chaotic behavior, at least classically.

Characterization of highly vibrationally excited molecules: Even for small molecules, large amounts of internal energy will produce quantum mechanical levels, or classical

trajectories, that are both difficult to calculate accurately, and hard to characterize after the calculation.

The characterization of isomerization rearrangement in clusters: Under what conditions are multiple minima, with not largely different energies accessed, in clusters?

Calculation of photodissociation and ionization of polyatomic molecules: Of special interest in this area is the implication of using femto-second lasers and other formerly exotic interactions of light with matter.

Calculation of quantum reaction dynamics beyond three atoms: Quantum reaction dynamics for three atom systems are being done with some level of regularity. However, further work needs to be done on how to expand this beyond three atoms.

Calculation of absorption and reaction dynamics on clusters and surfaces: This work is just in the beginning stages.

Fitting and sensitivity analysis of potential energy surfaces: What parts of large dimensional polyatomic or potential energy surfaces need to be calculated in order to get useful predictions of experimental quantities? After the potential energies at specific geometries are calculated, or during calculation, how are they conveniently represented as a multi-dimensional surface?

MODEL AND SIMULATION LEVEL

On the modeling and simulation level, there was less discussion. The following are some examples of the items discussed. It is in no way a comprehensive list.

Soot formation

There are a number of models these days for soot formation, but they are not all consistent with one another or with the experimental results. There is certainly a need for a comprehensive and consistent model.

NO_x processes

While there is considerable information at the detailed kinetics level of NO_x reactions, more work can be done in the actual simulation of practical devices to identify crucial information still lacking.

Coal combustion

There are aspects of coal combustion regarding gas surface interactions about which no information is presently available.

Sensitivity analysis

Although sensitivity analysis has already been incorporated into simulation studies, there is still a need to integrate sensitivity analysis still further, and to identify crucial molecular level information, which can be given to the chemical dynamics side of this proposal for investigation.

RESOURCES NEEDED FOR RESEARCH OPPORTUNITIES

If these are the research opportunities, what kinds of resources are needed? As currently written, the proposals call for:

1. The establishment of a major visitors program modeled on either of the existing programs at the CRF, which is experimental, or at JILA. Envisioned are two kinds of visitors: visitors for whom there is no real salary support; and fellows for whom there is a sabbatical salary support as is the case at JILA.
2. A relatively modest staffing increase on the order of two staff members and a post-doc at the CDRL site, and several numerical analysts and a few post-docs at the Sandia site.
3. The incorporation of existing groups, both at Sandia and at Berkeley, into either the CDRL at LBL, or the CCCS at Sandia.

We have recommendations as a committee at large on all three of these items.

Visitors program

The visitors program needs to be better balanced with the amount of staff available with whom the visitors will be interacting. Given the amount of permanent staff in the program, we thought a visitors program of approximately 15 visitors is appropriate. The numbers currently called for (30 or so) is probably too ambitious for the number of staff. Also, currently in the report, most of these visitors were going to be of the non-salary kind, and only a couple were going to be fellows. The group recommends that there be more of a mix of fellows in the visitors program and that there would be fellows at both institutions. This was considered very important, especially since the motivation is to be able to go from fundamentals all the way to practical simulation is a major purpose of the theory. Furthermore, in order to more actively integrate the two programs, we recommend priority be given to those visitors that bridge the chemical dynamics and combustion programs, who may have offices, or spend part of their time, at both institutions. Finally, in the text of the current proposal, there is an external visitor category, that is a person who would come to institution, write up his own work under his name with no collaborative interaction. Without exception the members of the group agreed the program does not want this type of visitor. The program wants

collaborative visitors who will take advantage of the scientists that are present, both experimentalists and theoreticians, not ones who want to only do their own work.

Staff increases

In order to have an effective visitors program, we felt there has to be a user friendly person, someone who will integrate the visitors into the hardware and software platforms that exist at whatever site they visit. This is not necessarily a full-time staff member but someone who is recognized as a resource for visitors. In addition, some staff increases are in the form of post-docs, and priority could be given to post-docs who are shared by the two institutions which will help bring them together.

Incorporation

There could be some mixture of the two groups by having joint appointments. People who have official appointments in both the CDRL and the CCCS compliment other calls for emphasis on joint seminars and workshops.

Resources

With a visitors program of 15 people, and the research opportunities that are available, what kind of equipment is necessary in order to have an effective, collaborative visitors program? For this program the equivalent of the highest generation computer is needed. That would be something like an 8-processor YMP if purchased tomorrow. That is a magnitude greater than what is currently recommended in the proposal. It is not necessary that the computer power be in the form of one kind of computer, or just one single highest generation computer, but that the equivalent power is available. It could be mixed between computers that can handle, and process, vanilla code very rapidly, or it could be a mixture of computers that have relatively unusual architectures which encourage algorithm optimization, in return for a large ramp up in speed. The computer could be bought, leased, or the time could be purchased. It is not necessary that it be located at either institution.

It can be located anywhere in the country, as long as there is good communication. Finally, when this effort goes on line, several years from now, the highest generation computer may not necessarily be the 8-processor YMP. It is possible in three or four years that power of greater magnitude than the present 8-processor YMP can be thrown at this problem

RESULTS OF THEORETICAL EFFORT

The end results of the theoretical effort would be:

1. Specific applications, or calculations, for comparison to a particular experiment or simulation of a particular process.
2. Methods that can be disseminated throughout the chemistry community. The visitors would go back to their own institutions and use these new methods on specific problems.

The end result of the theoretical effort would not be the export of computer cycles. The effort is not supposed to be a computer operation in which people can call up, do their own work, and not be physically present at CCCS or the CDRL. It is to be a collaborative interaction with the resident scientists.

ISSUES TO BE DISCUSSED

There were many issues not discussed due to insufficient time. These issues are very important.

A. Integration

What is the connection between the theory discussed here and other outside efforts? There are other major labs, e.g. PNL, that are interested in the subject of toxic junk being thrown into the environment. Other large groups, e.g. NASA, Ames, our program at Argonne, and many universities, are also interested. IBM has a program in parallel computing. All these groups are working on aspects in theoretical computations in both methods development and specific applications, that are relevant to the work proposed here. The proposed theoretical effort must be integrated into this existing effort, so that we do not end up re-inventing the wheel at each institution. Finally, is there going to be any benefit to individual researchers who are not likely to be visitors? For instance, will there be an organized method of disseminating software? That could be one way to integrate people who are unable to be physically present to take advantage of the visitors program. The last item of integration is to get back to some of the first comments made. How to aggressively reach the full combustion community and how to communicate with combustion scientists who do not recognize this proposal as a combustion proposal are questions that remain to be answered.

B. Hardware/software

The mini supercomputers and workstations proposed for the permanent groups were not discussed. Scientists like electronic structure theorists, or chemical dynamicists, added to the program in the proposed modest staff increases, would have an interest in determining what kind of mini-supercomputers/workstations mix should be installed. Flexibility in that regard is important. Finally, the role of visualization and its impact on the day to day scientific activity, was not discussed. Depending on the impact, what kind of computer support should it receive?

III Appendix A

Attendees List

CDF April Workshop Attendees

Martin F. Jarrold
AT&T Bell Laboratories

Mark A. Johnson
Yale University

Robert J. Kee
Sandia National Laboratory

Kwang-Je Kim
Lawrence Berkeley Laboratory

Mike Koszykowski
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Donald Lucas
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Jay Marx
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Carl F. Mellus
Sandia National Laboratories

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C. Bradley Moore
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Cheuk-Yiu Ng
Ames Laboratory

Robert A. Perry
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David J. Rakestraw
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Roberta P. Saxon
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Charles V. Shank, Director
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Yuen-Ron Shen
Lawrence Berkeley Laboratory

Anthony Siegman
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Reed J. Jensen
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Jane Rice
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Richard J. Saykally
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Chun-Ching Shih
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J. A. Keizerle
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Masato Koike
Lawrence Berkeley Laboratory

Allan Laufer
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Kopin Liu
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Lawrence Livermore National

Larry Rahn
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Volke Sailer
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CDF April Workshop Attendees

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Peter Chen Harvard University	Hao Lin Chen Lawrence Livermore National	Robert K. Cheng Lawrence Berkeley Laboratory
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