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Combustion Dynamics Facility

Scientific Program Summary

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Lawrence Berkeley Laboratory
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Sandia National Laboratories
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FOREWORD

This document describes the research program, experimental facilities, and operations plan proposed for the Combustion Dynamics Facility (CDF), a joint proposal by the Lawrence Berkeley Laboratory (LBL) and Sandia National Laboratories (SNL), in support of the Department of Energy's Chemical Sciences Division. The purpose of this scientific program summary is, in part, to acquaint a broad range of investigators with the facilities that would be available at the CDF and to describe the new capabilities that the combustion and chemical dynamics research communities would thus enjoy. At the same time, it is hoped that this summary will stimulate further discussion among potential users of the CDF. We encourage the broadest possible involvement in the continuing discussions that will lead to refined descriptions of the science to be done at the CDF, to further definition of the necessary experimental facilities, and to the most responsive configuration of the user program.
Combustion Dynamics Facility

Scientific Program Summary

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1. EXECUTIVE SUMMARY

In support of DOE's national role in combustion research, the Lawrence Berkeley Laboratory (LBL) and Sandia National Laboratories (SNL) are proposing a major initiative—the Combustion Dynamics Facility (CDF). The CDF comprises three elements: enhancement of the existing Combustion Research Facility (CRF) at SNL, establishment of the Center for Computational Combustion Science (CCCS) at SNL, and construction of the Chemical Dynamics Research Laboratory (CDRL) at LBL. Collectively, the CDF will serve as a national user facility devoted to advancing DOE's energy sciences mission to enhance the efficiency of combustion processes while minimizing such undesirable effects as the production of pollutants.

At the CDRL, research will focus on elucidating the production, structure, and reactivity of critical reaction intermediates and transient species, and on the dynamics of elementary chemical reactions. Work at the CRF will emphasize optical diagnosis of combustion, studies of chemical kinetics and reacting flows, and complementary studies in chemical physics. The CCCS will serve as a focus for computational support of the CRF and will supplement theoretical efforts at the CDRL. Both LBL and SNL will develop the most advanced instrumentation that can be brought to bear on research topics pertinent to combustion issues, and this equipment will be made broadly available to combustion and chemical physics researchers.

The result of these efforts will be new insights into the elementary reactions involved in hydrocarbon combustion, the structure and dynamics of highly excited molecular species and reactive intermediates, and molecular energy flow processes, all of which are critical to advances in combustion technology. This new knowledge will be applied to the modeling and prediction of combustion phenomena and other complex chemical processes and to the development of advanced combustion systems.

The CDF will offer unparalleled experimental resources for users from around the nation to study fundamental and applied combustion processes. At the CDRL, a new advanced infrared free electron laser (IRFEL), molecular beam apparatus, dedicated chemical-physics synchrotron radiation beamlines at the Advanced Light Source (ALS), and advanced lasers will be made available. They will be used for dynamical, spectroscopic, and structural studies of many types of
1. EXECUTIVE SUMMARY

highly reactive molecules, including radicals, clusters, and unusual transient species. As indicated schematically in Fig. 1-1, the user facility will allow, for the first time, the integrated and simultaneous use of dedicated IRFEL and ALS beamlines for pump-probe experiments and for experiments with crossed molecular beams. Using the ALS as the pump and the IRFEL as the probe, researchers will be able to study the vibronic structure of highly excited and superexcited molecules. Used in the IRFEL pump–ALS probe mode, the combined technologies will provide a variety of new information:

- Badly needed IR spectra of transient species for combustion diagnostics
- Energetics and reactivity of free radicals
- New vibrational spectra and insights into the dynamics of ions and clusters
- Insight into achieving regioselective photochemistry

Figure 1-1. A schematic drawing suggesting the unique interrelationships among the experimental facilities proposed for the CDRL at LBL, and the types of experiments that will be significantly advanced.
In addition, the time structure of the ALS and the IRFEL, and the ability to synchronize their outputs, will allow picosecond time-resolved studies of the dynamics of the dissociation of radicals and clusters, as well as studies of energy redistribution and molecular rearrangement on surfaces. A parallel theoretical effort will pursue new quantum calculations and develop new potential energy surfaces to assist in the interpretation of experimental results and to guide the direction of future experimental efforts.

At SNL advanced femtosecond and multiple-beam laser systems and forefront computational capabilities will enable researchers to study ultrafast processes in combustion and to undertake two- and three-dimensional imaging studies of the physical and chemical properties of turbulent reacting flows. As suggested in Fig. 1-2, a close relationship between the basic research program and new user facilities at LBL and the more applied research program and complementary facilities at SNL will ensure a synergism that will speed the transfer of fundamental research to practical applications. A notable example is the development of optical diagnostics. The CDRL facilities at LBL can be brought to bear on spectroscopic investigations of radicals and other transient species important in combustion. The IRFEL, for example, will allow scientists to excite and study the internal modes of transient species in a way that simulates the combustion environment. In addition to expanding our understanding of the properties of these species, the information will provide a much needed database that is crucial for the broad application of optical diagnostic probes for species in flames. Collaborations between staff and visitors at LBL and those at Sandia will result in rapid development of optical diagnostics for polyatomic species.

Management responsibility for the CDF will reside with a director at each site. A Steering Committee of external advisors will be appointed to provide advice on broad scientific and policy issues, and a Program Review Panel of scientific peers will ensure that the facilities are used for the most innovative and productive lines of research. The managerial approach for the CDRL is designed to promote multi-investigator chemical physics research, coupling experimental and theoretical efforts; to build a strong visitor program; and to advance the application of new instrumentation for molecular studies. SNL has operated the CRF successfully for the chemistry and combustion community since 1980; its management and operations can be integrated into the CDF with little change.

The CDF management will be oriented toward hosting visiting scientists, and its user facilities will be made available to all qualified investigators. Scientific and technical staff will be available to support collaborations of external users and in-
Figure 1-2. An indication of the synergism within the multisite CDF that could be brought to bear on such problems as the combustion of aromatic hydrocarbons, a process that is poorly understood and yet likely to be important in the combustion of low-grade fuels. The development of new optical diagnostic techniques is an essential element in this scenario.
house research personnel. Workshops and training seminars will be conducted to advance research progress and provide orientation to new users and graduate students.

Additional details regarding the operations plan for the CDF are provided in Section 4. New CDF facilities are described in Section 5. The heart of this document, however, is the proposed science, which is presented in Section 3, following a brief introduction.
2. INTRODUCTION

2.1 BACKGROUND

Highly productive modern scientific research requires broad and vigorous interaction among theorists, experimental scientists, and instrumentation engineers and physicists. Like the United States, West Germany and Japan have made tremendous scientific and technological advances using this approach in recent years. Advancing countries, such as Taiwan and Korea, are patterning their research programs on a similar model.

The Combustion Dynamics Facility (CDF) is being proposed jointly by the Lawrence Berkeley Laboratory (LBL) and the Sandia National Laboratories (SNL) to provide advanced national user facilities aimed at maintaining U.S. scientific and technological leadership in combustion chemistry research and chemical dynamics studies. Such research is crucial in sustaining the international competitiveness of U.S. energy and high-technology industries.

The LBL effort, embodied in the Chemical Dynamics Research Laboratory (CDRL), will focus on elucidating the production, structure, and reactivity of critical reaction intermediates and transient species, and on the dynamics of elementary chemical reactions. The Sandia effort, based at an enhanced Combustion Research Facility (CRF) and a new Center for Computational Combustion Science (CCCS), will emphasize optical diagnosis of combustion, studies of chemical kinetics and reacting flows, and complementary studies in chemical physics. Research at the CDRL and CRF will result in basic new knowledge about elementary reactions involved in hydrocarbon combustion, the structure and dynamics of highly excited molecular species and reactive intermediates, and molecular energy flow processes, all of which are critical to advances in combustion technology. Through the CCCS, this knowledge will be applied to the modeling and accurate prediction of combustion phenomena and other complex chemical processes and to the development of advanced combustion systems.

Such detailed understanding of the chemical behavior of molecular species that are highly reactive, severely strained, or unstable, as well as molecules in excited electronic and vibrational states, is unavailable from conventional chemical experiments. It will be the purpose of the CDF to advance our knowledge in this
important area by launching an intense experimental and theoretical effort. The approach is to make a concerted attack that entails basic investigations at the molecular level, performed at LBL, and a systems study of complex combustion and reacting flow systems, using advanced imaging and diagnostics techniques at SNL. Focused, multi-investigator collaborations of external users and in-house research personnel will be supported at these facilities by a dedicated scientific and technical staff.

2.2 INTEGRATED COMPLEMENTARY TECHNOLOGIES

Recent national reports and symposia, including the Workshop on Opportunities for Chemistry Related Combustion Science, held in July 1986, and the Workshop on Chemical Reaction Dynamics, held in November 1988, have identified the needs and opportunities for advances in spectroscopic techniques, free electron lasers, synchrotron light sources, conventional lasers, molecular beam methods, and imaging and computational techniques to advance research in the field of combustion and chemical reaction dynamics. Several important and challenging areas are especially ripe for investigation: the chemical reactivity, structure, and spectroscopy of polyatomic radicals, reaction intermediates, clusters, and unusual transient species; the mechanisms of soot formation and destruction; ignition processes; nitrogen chemistry; the dynamics and mechanisms of the decomposition of aromatic molecules under collision-free conditions; reactions at surfaces; unsteady combustion phenomena; characterization of flame-generated materials; and studies of flames at high pressure and temperature. The workshops emphasized that investigations in these areas require the utilization of complementary and integrated advanced technologies.

Infrared Free Electron Laser. One such major new technological opportunity is the infrared free electron laser (IRFEL), which can be a powerful tool for studying molecular excitation and dissociation. Significant scientific opportunities were identified in a recent workshop. A dedicated IRFEL that has all the required characteristics for chemical sciences research is an essential part of the CDF and will be fabricated and installed at LBL as a part of the CDRL. This will open new studies using the technique of infrared multiphoton excitation and dissociation under collision-free conditions. This powerful technique has been limited so far to those molecular species that can be excited by the CO$_2$ laser, which has limited tunability. With its broad tunability, the IRFEL will provide access, for the first time, to practically all molecular species, containing elements across the periodic table. Using the IRFEL, chemists will be able to probe basic molecular dissociation
processes; produce unusual transient species such as organic free radicals, reactive intermediates, and radical-containing clusters; and study chemistry and spectroscopy on surfaces, as well as in the gas phase, thus providing necessary data for flame diagnostics and other combustion research.

**Advanced Light Source.** Another technology that promises rich rewards in combustion research is the Advanced Light Source (ALS), an intense synchrotron radiation source now under construction at LBL and scheduled for operation in 1993. The high flux and especially the high brightness of this source offer new possibilities in photoionization, photodissociation, and photoelectron studies of polyatomic molecules and radicals.

**Lasers.** Still another major technology is the femtosecond laser. Being constructed at SNL as part of the CRF, this laser system will extend research capability into the regime required for studying ultrafast processes important in combustion physics and chemistry, and it will make possible new approaches to three-dimensional imaging of combustion phenomena. Its use will focus on studying intramolecular vibrational relaxation, the dynamics of molecular photodissociation, the course of molecular collisions, and other phenomena that form the basis for a truly fundamental understanding of combustion. Time-resolved, two-dimensional scattering images collected as these pulses propagate through a combustion system will yield three-dimensional information about the structure and composition of the medium, with high spatial resolution. Three-dimensional imaging of turbulent reacting flows will be an important element of the work performed.

A second powerful new tool under development at the CRF, the multiple-beam Nd:YAG/dye laser system, will make a major impact in studying turbulent reacting flows and will also provide important new capabilities for chemical physics experiments. The new system will allow individual laser pulses to be timed arbitrarily with respect to one another, to generate anything from a bunched pulse containing ten times the energy of a single laser's output, to a train of equally spaced pulses propagated at 100–200 Hz. The fast-framing mode of operation, in which successive pulses are spaced by a time appropriate for studying the evolution of a turbulent medium, will be an especially powerful tool for investigations of chemically reacting flows. Many important diagnostic applications of this new laser system will emphasize the generation of multiple two-dimensional images, scanned in time to construct a movie of a turbulent flow, or scanned in space to generate an instantaneous three-dimensional image of the flow. Research examples include measurement of scalar dissipation in flames, simultaneous imaging of several species in flowing media, and studies of ignition and the propagation of resulting
flame kernels. For studies in chemical physics, such as the detection of the products of radical-radical reactions, the lasers will deliver different wavelengths so that several species or quantum states can be probed simultaneously.

2.3 RESEARCH FOCUS AND GOALS

The recent workshops also identified a variety of important topics within DOE's mission to enhance the efficiency of combustion processes while minimizing undesirable effects such as the production of pollutants. The broader issues of fundamental studies will be tackled at LBL, while macroscopic phenomena will be studied at SNL. Complementary, but not overlapping, work at SNL in the area of chemical physics will provide a direct link between the programs. Several research avenues are described in Section 3, as a stimulus for further study and discussion.

Broadly, however, the research objectives of the CDRL will be (i) to determine the structure and chemical behavior of highly reactive polyatomic radicals and unusual transient species, (ii) to provide microscopic details of the mechanisms and dynamics of elementary chemical reactions and primary photodissociation processes, (iii) to probe the nature of intra- and intermolecular energy relaxation, (iv) to search for bond-selective or mode-selective means to modify and manipulate chemical reactivity, (v) to establish a sound theoretical foundation to understand chemical reactivity and to guide experimental efforts, and (vi) to develop novel methodologies and tools to tackle important, currently unsolvable problems in chemical dynamics. These goals will be achieved using a host of experimental and theoretical-computational approaches.

At the CRF and the CCCS, the focus will be on (i) studying ultrafast processes—such as intramolecular vibrational relaxation, the dynamics of molecular photodissociation, and the course of molecular collisions—that form the basis for a truly fundamental understanding of combustion, (ii) obtaining with high resolution both two- and three-dimensional images of the physical and chemical properties of turbulent reacting flows, (iii) generating detailed information on kinetics and dynamics in systems for which appropriate diagnostics are not now available, (iv) using the results of fundamental theoretical and experimental research to develop comprehensive computational building blocks in areas such as thermochemistry, chemical kinetics, and turbulent fluid flow, (v) assembling from these building blocks predictive models of real combustion processes, and (vi) using these models to improve the performance of such practical devices as coal-fired boilers and internal combustion engines.
2.4 Project Scope

At LBL the CDF provides for the integrated and simultaneous use of an IRFEL, the ALS beamlines, and advanced laser systems for experiments in the main hall of a new CDRL building adjacent to the ALS. The laboratory will enable the flexible arrangement of experimental equipment, instrumentation, and computer interface systems. The CDRL will be managed to host visiting scientists in a manner that has proven to be highly successful at the CRF. Its user facilities will be made available to all qualified investigators, either in collaboration with resident researchers or for use in independent research. Annual summer workshops and training programs will be conducted to discuss research progress and provide orientation to new users and graduate students.

At SNL two new laser systems will become part of the CRF, where they will advance the technology of optical diagnostics and imaging of turbulent reacting flows in order to probe chemical and fluid-mechanical phenomena with greater resolution in time, energy, and space. These new facilities will markedly enhance the ability of visitors and staff at the CRF to probe combustion phenomena with the resolution required to make further progress in established directions and to open completely new lines of attack on important problems. The project provides for a femtosecond laser system and a multiple-beam Nd:YAG/dye laser system. The lasers will be housed in a new laboratory building with offices to accommodate new visitors and to improve scientific interaction of staff and visitors.

It should also be emphasized that both theory and modeling will play significant roles at the CDF. Highly productive research requires broad and vigorous interactions among theorists and experimentalists. Further, participants at meetings such as the Workshop on Opportunities for Chemistry-Related Combustion Science discussed computing issues and concluded that only the most up-to-date computational capabilities are adequate for forefront research in chemical physics and combustion sciences. The CDF will make these capabilities available to all its users.

The CDRL will provide a supportive environment for interactions between theorists and experimentalists, and state-of-the-art computing resources will be available. To enhance interactions with experimentalists, offices will be provided for 5 in-house theorists and 5–10 visiting theoretical chemists, in close proximity to the experimental efforts. For the ab initio quantum chemistry and dynamics calculations that will be the focus of CDRL-based research, state-of-the-art workstations and/or super-minicomputers will be provided, together with 1.5-Mbit
communications link to SNL's central supercomputer facility. High-speed links to the UC Berkeley campus will also be installed.

At SNL the CCCS will further consolidate existing cooperative efforts between experimentalists and theoreticians at Sandia, as well as provide a national focus for computational studies in the combustion sciences. The long-term goal of the CCCS will be the development of predictive models of combustion processes. Such theoretical developments require a comprehensive computing environment that comprises several key elements. Most important, adequate computational horsepower must be harnessed to solve the complex mathematical problems involved. In the near term, this is best done by using conventional supercomputers. In the longer term, this computational power will probably be provided by the emerging technology of massively parallel supercomputers. Proximity to the computers is a second element. Activities within the CCCS will emphasize multidimensional time-dependent modeling activities. To provide adequate visualization of the time-dependent information produced in these calculations requires that the computer users, both in-house researchers and visitors, be close to the supercomputer itself.

2.5 PRACTICAL BENEFITS

The close relationship between the programs at LBL and at SNL, together with the CRF's strong ties to industry, will ensure a synergism that results in the rapid transfer of fundamental work to practical application. A notable example is the development of optical diagnostics. At present, optical techniques are recognized as best for probing reacting media in a nonperturbing way. Their application is limited, however, by the fact that the spectroscopic database necessary for their application exists for only a very few species containing more than two atoms. The CDF will be a unique facility in which unparalleled resources can be brought to bear on spectroscopic investigations of radicals and other transient species important in combustion. The IRFEL will, for example, allow scientists to excite the internal modes of transient species in a way that simulates the combustion environment. The information obtained will be useful in its own right, in expanding our understanding of the properties of these species, but it will also provide a crucial database for the development of optical diagnostic probes for species in flames. Collaborations between staff and visitors at the CDRL and those at the CRF will result in rapid development of optical diagnostics for polyatomic species.
Soot is an important combustion-generated pollutant. The CDRL will have a strong research program that investigates the spectroscopy of organic and inorganic clusters. It will complement CRF studies of the spectroscopy and reactivity of carbonaceous clusters. Both these efforts will couple strongly to more applied work at the CRF on low-pressure flames, in which scientists are determining the pathways by which small molecules grow to large ones on their way to soot.

The oxides of nitrogen, NO$_x$, are also important pollutants. The CRF has a variety of kinetics, flame, and modeling efforts directed at understanding their formation and destruction in combustion systems. RAPRENO$_x$, a chemical process that eliminates NO$_x$ from exhausts, is a direct result of work at the CRF. Theoretical and experimental efforts at LBL will complement these studies.

The necessity of avoiding destructive engine knock now establishes an upper limit on the compression ratio of gasoline-powered engines, which, in turn,limits their efficiency. At the CRF, there is a variety of research aimed at generating a better understanding of knock. The CDF will thus provide an excellent setting for collaboration between users at LBL and those at SNL to obtain better optical diagnostics for the appropriate precursor species. It will make possible many new, basic studies aimed at controlling flames and/or individual combustive reactions.

In addition to providing unique and important opportunities for a major thrust into the understanding of the dynamics of the combustion process, the CDF facilities will be applicable to the broader field of chemical dynamics in general. Combustion studies will benefit from techniques and spectroscopic information derived from experiments designed to study dynamical processes in the condensed phase—in novel solid-state materials, semiconductors, metal clusters, inorganic crystals, and polymers. These experiments broaden the utility of the facilities, and the experiments taken together will provide unmatched U.S. leadership in the study of dynamical chemical processes for many years to come.
3. RESEARCH OPPORTUNITIES

This section offers a provisional glimpse of the unique research opportunities to be afforded by the Combustion Dynamics Facility—especially those that demand the confluence of technologies described in Section 2. The research descriptions that follow were compiled from the contributions, some more formal than others, of many scientists. They include both theoretical and experimental studies of gas- and condensed-phase phenomena, with an emphasis on understanding transient species such as free radicals, clusters, and ions, especially those relevant to combustion processes. These descriptions are intended not as a final summary of research to be performed at the CDF, but rather as a snapshot of current thinking and a stimulus for further scientific discussion.

The major sections that follow cover photoelectron-photoion processes (§3.1); intramolecular dynamics and primary dissociation processes (§3.2); cluster and ionic beam processes (§3.3); spectroscopy, energetics, and dynamics of free radicals (§3.4); surface and condensed-matter applications (§3.5); research on combustion diagnostics (§3.6), and complementary theoretical and computational research (§3.7).

3.1 PHOTOELECTRON-PHOTOION PROCESSES

3.1.1 High-Resolution Photoelectron and Fluorescence Studies

High-resolution photoionization and photoelectron-photoion coincidence (PEPICO) experiments advance our understanding of the fundamental principles of chemical kinetics through the investigation of the dissociation dynamics of AB$^+ \rightarrow A^+ + B$, where AB represents any molecule. In addition, energetic and structural information about transient species, such as the free radical B, can be derived from the results. The free radicals produced in the dissociative ionization process are often structurally different from those formed by standard pyrolysis methods, so this approach complements the standard methods of free radical chemistry. Free radicals can also be investigated by threshold photoelectron spectroscopy (TPES). This provides information about the vibrational structure of the free radical and its ion.

Threshold Photoelectron Spectroscopy. One of the most effective methods for obtaining high-resolution photoelectron spectra is by the technique of TPES, in
which the electron energy analysis is achieved by time-of-flight (TOF) analysis of the low energy electrons [1, 2]. When the ALS is operated in the 8-bunch mode, with 82 ns between bunches and with up to 20 mA per bunch, the expected photon pulse width will be about 50 ps. Calculations show that extraction of the electrons by an electric field of 1.0 V/cm, a 7.5-mm acceleration region, and a 15-mm drift region, results in a zero-energy electron TOF of 58 ns. The longest TOF will be for electrons that are ejected in the "opposite" direction and must be turned around by the 1.0-V/cm electric field. Their TOF will be 75 ns. Under these circumstances, the resolution for zero-energy electrons will be about 0.3 meV when using a time window of 200 ps. This should be readily achievable with suitably fast electronics and detectors [3]. A resolution of 1 meV over the entire energy range from the ionization potential to 30 eV will reveal new structure for nearly all molecules investigated.

High-resolution TPES can also be coupled to a two-color experiment. The IRFEL, time synchronized to the ALS, can be used to excite an IR mode of the sample molecule. The excited molecules will contain one quantum of vibrational energy in an asymmetric mode. When these are ionized by the synchrotron radiation, the ions are produced with vibrational energy in the asymmetric modes. These are the modes that cannot be excited from the vibrational ground state. Thus, a whole new set of vibrational modes in the ions can be investigated. The energies of these modes are frequently unknown, even in some simple ions such as CO$_2^+$. The signal level should be high. A cold beam of molecules has most of its molecules in the ground vibrational and rotational levels. Thus, a large fraction of the molecules can be excited with the high-intensity FEL [4]. The two-color ionization signal can be monitored by measuring the difference between the IR-on and IR-off signals.

Photoelectron-Photoion Coincidence Experiments. Two of the major problems in PEPICO experiments carried out so far is the low energy resolution (typically 20–40 meV) and the broad thermal energy distribution of the room-temperature sample gas (typically 80–200 meV) [5]. A few PEPICO experiments have been carried out with better energy resolution [6] or with a cooled sample gas [7], but not with both. The use of a cold molecular beam and the excellent electron energy resolution will solve both of these problems. It should even be possible to investigate ion chemistry with some rotational energy resolution by using the IRFEL as a method for selecting the rotational energy in a manner similar to that used by Kuhlwind et al. [8]

The types of reactions to be investigated are ionic dissociation reactions of metastable ions. The 50-fold increase in internal energy resolution provided by the
ALS will certainly reveal new information about these complex reactions. In particular, it would be most interesting to investigate the dissociation of closed-shell ions—ions that can be formed by photoionization of free radicals. It has been evident for some time that ions are far more likely to dissociate statistically than are neutral molecules. The latter often dissociate directly on a repulsive excited potential energy surface. On the other hand, ions nearly always relax via internal conversion to the ground electronic state prior to dissociation. Is this a by-product of the unpaired electron, which causes excited electronic states to be more strongly coupled, or is it a by-product of the long range $1/r^4$ interaction potential? Studying the dissociation of such closed-shell ions as $\text{C}_3\text{H}_3^+$ and $\text{C}_5\text{H}_5^+$ would provide some clues.

It may also be possible to investigate ion-molecule reactions of such species as $\text{O}^+ (2D, 2P)$ or $\text{OH}^+(v)$ with various neutral collision partners. The trick is to prepare oxygen atoms and OH free radicals, and then to prepare the ions in selected states by PEPICO. These processes are important in plasma chemistry, where many excited species are present. Few such experiments have been done to date [9], because they require very intense sources and efficient methods for free radical generation. The CDE will be the ideal location for such experiments, since free radical production will be an area of major emphasis.

**Fluorescence Studies.** Ionization of molecules is only one of a number of decay paths available to super-excited molecules. Often, a more rapid process is dissociation to neutral fragments. These dissociation reactions, which are usually the sole decay route below the ionization limit, can compete with ionization even several eV above the ionization limit [10]. It has been demonstrated that the branching between dissociation and ionization is strongly dependent upon the electronic and probably rotational states of the super-excited neutral state [10]. These decay channels will be investigated as a function of the internal energy, with rotational resolution, by using the IRFEL as the initial excitation step. A specific rotational state $J$ of a molecule such as $\text{N}_2\text{O}$ can be populated by the IRFEL. Subsequent excitation by the synchrotron light will produce a super-excited state in the rotational states $J' = J \pm 1$. The dissociation channels can be monitored by dispersed fluorescence of the neutral decay products. Extensive fluorescence studies have been carried out at other synchrotron facilities by Poliakoff et al. [11] and Guyon et al. [12] The higher resolution, especially the rotational selection, available at the CDRL will advance this field significantly.
3. RESEARCH OPPORTUNITIES

3.1.2 Studies of Molecular Excited States

**Double-Resonance Experiments.** In the intermediate energy regime from 6 to 12 eV, synchrotron light sources with the intensity of the ALS will open important new avenues for studying spectroscopy and reactivity of highly electronically excited molecules. Resolved spectroscopic access to higher energies, provided by multiphoton laser techniques, has provided a glimpse of a fundamentally new class of dynamical processes that emerge with the selective population of molecular excited states near and above first ionization potentials [13]. The ALS will expand this view by orders of magnitude.

A principal strength of the ALS is its continuous wide tunability deep into the VUV and beyond. In this respect, it is ideal for surveying complete absorption spectra of higher molecular excited states. At the same time, the available high intensity and high spectral brightness of the ALS should enable the acquisition of such spectra at relatively high resolution in systems cooled by free-jet expansion.

Most importantly, at the ALS, this broadly tunable, high-brightness radiation will be delivered with a natural time structure that is ideal for double-resonance and pump-probe experiments. A sequence of laser and synchrotron pulses can be designed to focus on vibronic structure and intramolecular dynamics of high-lying electronic states. For the first time, routine measurements of VUV absorption spectra of molecules in selected vibrational-rotational levels will be possible.

A strong motivation exists for combining synchrotron radiation with laser light in two-color, state-selected excitation schemes. By double resonance, state-selected spectroscopy overcomes the principal limitation of conventional spectroscopic approaches to highly excited molecules, namely, the characteristic high densities of states. The now-widespread application of double-resonance methods to the laser spectroscopy of a handful of suitable systems [14] has been a major driving force in the surge of theoretical activity concerned with high-energy molecular structure and dynamics [15]. Pump-probe methods employing synchrotron radiation promise to generalize both experimental and theoretical efforts to cover the complete class of problems chosen on the basis of fundamental and practical importance, as opposed to experimental convenience [16].

A number of experiments are envisioned. Among the simplest is the acquisition of free-jet VUV absorption spectra over wide intervals below first ionization thresholds. Such experiments will be followed by the examination of individual features by analyzing the photoelectrons. This excitation method projects the VUV-prepared electronically excited state onto the manifold of
accessible ion vibronic states, much like the resolved emission spectrum of a first-valence excited state projects $S_1$ on the manifold of the electronic ground state. The identification of excitation states that have different limiting ion vibronic characters will prove useful in establishing routes to state-selected populations of ions for studies of state-to-state ion-molecule reaction dynamics, and as gateways to the production of autoionizing states.

Variations on this technique of synchrotron excitation followed by laser ionization can give valuable, highly selective survey information. Electron energy analysis can be used to acquire signal from processes that lead to specifically selected ion final states. For example, collecting electrons of only the highest accessible energy isolates transitions leading to the cation ground state. A synchrotron scan detected in this way registers only those VUV-prepared states that have significant oscillator strength for such transitions, an important subset of high-lying electronically excited states. Other techniques employing tunable probe laser radiation can easily identify two-color threshold transitions to specific ion rotational states, which can be used either to resolve electronic structure more finely, or to learn about state-resolved photoionization cross sections and ion rovibrational structure [17].

**Intramolecular Dynamics of Electronically Excited Molecules.** Internal conversion and intersystem crossings are two intramolecular processes of great importance in electronically excited molecules. The rates of fast internal conversion and intersystem crossing in many polyatomic molecules and radicals are not known because of experimental difficulties. The best approach to providing the missing information is to carry out photoelectron spectroscopy of excited molecules with picosecond laser systems. By using a tunable picosecond UV laser to pump the molecule and a second, fixed-frequency, visible laser to carry out time-of-flight photoelectron spectroscopy, it is possible to probe the conversion of electronic energy to vibrational energy by looking at the characteristic photoelectron spectra associated with specific electronic states of the molecules.

For very highly excited Rydberg molecules, similar experiments can be carried out using the ALS undulator beamline, with the IRFEL operating in the region of 3 μm, again using time-of-flight photoelectron spectroscopy. Synchronized operation of the ALS and the IRFEL will be required.

**XUV Absorption and Photoelectron Spectroscopy of Cations.** The application of intense monochromatic XUV radiation from the ALS to suitably prepared ion beams will open new fields of inquiry into the electronic structure and high-energy spectroscopy of cations. Moreover, with photon energies accessible at the U10.0
undulator or bending magnet ports, it will be possible to photoionize di-cations to doubly charged final states. Di-cations of small and large molecules are well-known in mass spectrometry, where their appearance in charge-stripping processes offers one of the few ways of distinguishing isomeric polyaromatic and aza-polyaromatic hydrocarbons. Many of the more stable and more interesting doubly charged ions are hydrocarbons, such as \( \text{C}_n\text{H}_m \) where \( n = 6, m = 2 \), etc. Polyaromatic hydrocarbons and their analogs have low second ionization potentials, making them copious producers of di-cations, the ion-molecule chemistry of which is entirely unexplored in combustion contexts. Substantial theoretical work is now under way on the structure and potential energy surfaces of diatomic and larger polyatomic di-cations, but very little spectroscopic information exists on rovibrational energy levels, bond lengths, and barriers to fragmentation.

Cold ion beams can be prepared by electron impact in free-jet expansions. After mass filtering, it will be possible to excite selected ions by XUV absorption to energies near and above second ionization thresholds. Intensities and positions observed in zero-kinetic-energy PES will give high-resolution information on di-cation rovibrational levels and cation photoionization cross sections. Photodissociation spectra of electronic states below second ionization thresholds will provide additional information on the high-energy electronic structure of cations, including the interesting question of Rydberg states built on doubly ionized cores. Translational spectroscopy of charge products will characterize fragmentation dynamics and the forces associated with long-range parts of ion-molecule potentials.

3.1.3 Experimental Equipment

Two experimental apparatus have been outlined as especially important for photoelectron-photoion studies. The first is a differentially pumped molecular beam source with two skimmers. The net pumping speed should be at least 5000 l/s in the main chamber and 1000 l/s in the differential chamber. This apparatus should be usable as both a normal cold gas source and a cold free radical source. The second apparatus is a 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. This chamber should be pumped by a 1000-l/s pump and should include a separately pumped beam dump. Portability and compatibility with other chambers at the CDRL are highly desirable features.
High-speed detection electronics with a rise time of about 100 ps are especially important for this station; they are the key to the unique ultrahigh-resolution (sub-meV) photoelectron detection capability to be made possible by the undulator beamline. Because commercial multichannel plate detectors are not fast enough, it will be necessary to fabricate detectors at the CDRL; specially fabricated preamplifiers are also likely to be required.

For pump-probe experiments, the picosecond tunable laser system described in Section 5.1.3 will be especially important. The most useful "off-the-shelf" laser systems include (i) a cw high-resolution IR laser, for example, an F-center laser or its future equivalent, (ii) a 1000-Hz excimer/dye laser system for triggering with zero-energy electrons, and (iii) a 1000-Hz excimer (ArF) laser for photolysis and radical preparation.

References: Photoelectron-Photoion Processes

3. RESEARCH OPPORTUNITIES


17. R.G. Tonkyn, J.W. Winniczek, and M.G. White, manuscript submitted.
3.2 **INTRAMOLECULAR DYNAMICS AND PRIMARY DISSOCIATION PROCESSES**

3.2.1 **Infrared Multiple-Photon Excitation**

Infrared multiple-photon excitation (IRMPE) has been used for over ten years as a method of exciting ground state molecules to high vibrational levels, which subsequently lead to unimolecular dissociation [1-4]. Lasers with adequate intensities and energy fluences are required for IRMPE in order to excite molecules with the necessary 5-30 quanta of radiation, in competition with radiative and collisional deexcitation. Advantages of excitation by IR radiation include a collisionless environment, species selectivity, and control over the extent of excitation. These properties have been used to study the dynamics and complex mechanisms of unimolecular dissociations of a variety of molecules, clusters, and ions. In some cases, particularly ions and clusters, the very nature of the methods of production and storage preclude conventional thermal excitation. Infrared excitation allows the thermal reactions of these novel species to be studied, thus providing important thermochemical and kinetic data. The general applicability of IRMPE for exciting molecules has been limited by the relatively few wavelengths available from high-intensity pulsed lasers (2.5-4 μm from optical parametric oscillators, 9-11 μm from CO₂ lasers). A continuously tunable IRFEL with sufficient intensity and energy fluence to drive multiple-photon processes would allow IRMPE experiments on a complete range of molecules, including organic, inorganic, and organometallic species. Only with a tunable intense radiation source can chemical trends be explored in many classes of materials.

From data taken with conventional lasers, product yields can be estimated for a comparable IRFEL experiment. Using a Nd:YAG-pumped optical parametric oscillator (OPO, 8-ns FWHM, 5-10 mJ/pulse, 6-Hz repetition rate) focused to a spot size of 10⁻³ cm² and focal volume of 10⁻³ cm³, the fraction of irradiated molecules dissociated per pulse is typically 10⁻³ for propylene, C₃H₆ [5]. For a diffraction-limited IRFEL producing 100 μJ/pulse, it should be focusable to a spot size of 3 x 10⁻⁵ cm² to produce nearly the same fluence as used in the OPO experiments (0.5-5 J-cm⁻²). Assuming a focal volume of 3 x 10⁻⁶ cm³ (area = 3 x 10⁻⁵ cm², length = 0.1 cm) and 1 Torr of sample, a dissociation efficiency of 0.1% per pulse in the irradiated volume produces (3 x 10⁻⁶)(10⁻³) = 3 x 10⁻⁹ Torr-cc = 1 x 10⁸ product molecules per pulse. To produce 10⁻² Torr-cc of total products would then require 3 x 10⁶ pulses. For an IRFEL producing 10⁵ micropulses per second, the experiment requires 33 seconds of irradiation. For the OPO experiment, 10⁻² Torr-cc of product requires 10⁴ pulses or 30 minutes. 10⁻² Torr-cc is approximately a factor of 100 above the minimum quantity detectable by packed-column flame ionization gas.
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chromatography. The low conversion per pulse means that slow diffusion out of the irradiation zone is not a problem. The reactant concentration is essentially constant and very few products will be subsequently dissociated. In a molecular beam experiment, IRFEL photons can be focused in such a way that during a macropulse of tens of microseconds all the molecules that travel several millimeters in the beam will be excited by the train of micropulses. A CO$\text{}_2$ laser pulse can follow to induce dissociation of the excited molecule.

An approach that avoids collisional quenching of slow reactions is to probe reaction products shortly after excitation. Unlike collisional quenching, a spectroscopic probe has the advantage of not perturbing the system. Using VUV from the ALS, $10^{14}$ photons per second are expected. This yields a photon flux of $6 \times 10^9$ photons/cm$^2$/micropulse. Assuming the same repetition rate as the IRFEL ($10^5$ per second in this example) and a photoionization cross section of $10^{-18}$ cm$^2$, $10^8$ products per micropulse yields $(10^8$ molecules/micropulse)$\cdot(10^5 \text{ micropulses/s})$ $(6 \times 10^9$ photons/cm$^2)(10^{-18} \text{ cm}^2) = 6 \times 10^4$ ions/s, which is easily detectable.

Tunable, intense, picosecond IR radiation will ultimately allow a broad range of molecules to be examined over a wide range of reaction times. Such an IR source will allow spectroscopic studies of transient species, a new understanding of ground state unimolecular reaction kinetics and thermochemistry, and possibly the derivation of propensity rules for intramolecular selectivity by IRMPE. The unique capability of an IRFEL at the CDRL lies in the combination of tunability, high energy, and short pulse length in the same device, which can be synchronized with the UV or VUV pulses from the ALS. These characteristics are not currently available in any conventional laser source.

At the CDRL, a dedicated state-of-the-art molecular beam apparatus is planned for photofragmentation translational spectroscopy in order to investigate hydrocarbon dissociation, especially the aromatic hydrocarbons, using infrared multiple-photon dissociation (IRMPD) with the IRFEL. In addition to dissociation processes of hydrocarbon molecules, the chemical and spectroscopic knowledge that will be accumulated by use of the IRFEL will have a great impact on our understanding of the important field of combustion chemistry.

**Primary Photodissociation Processes of Hydrocarbons.** In high-temperature combustion processes, dissociation of hydrocarbons precedes the oxidation processes; thus, it is necessary to understand thermal dissociation processes of hydrocarbons into smaller molecules and radicals. By using the IRFEL and synchronizing the macropulses with a TEA CO$\text{}_2$ laser, it is possible to dissociate almost all medium-size (~6–10 atoms) and large molecules using IRMPD in a molecular beam.
Two examples of experiments that could not be done with a fixed-frequency CO\textsubscript{2} laser include the dissociation of aromatic hydrocarbons and the dissociation of CH\textsubscript{2}=CH–C≡CH. The dissociation of aromatic hydrocarbons often involves extensive isomerization processes prior to dissociation, and they are not well-understood. The IRFEL will allow excitation of aromatic hydrocarbons that do not absorb CO\textsubscript{2} laser photons. The dissociation dynamics of CH\textsubscript{2}=CH–C≡CH will reveal the important reaction mechanisms of addition reactions involving two acetylenes. Whether the formation of CH\textsubscript{2}=CH–C≡CH\textsubscript{3} involves the initial isomerization of CH≡CH to CH\textsubscript{2}=CH–C, or occurs through a molecular reaction to form the ·CH≡CH–CH=CH· diradical, followed by the 3–1 hydrogen atom transfer, can be answered by measuring the translation energy distribution of the products of the reverse reaction. This experiment will require use of the IRFEL, a pulsed CO\textsubscript{2} laser, and the ALS U10.0 undulator beam without the monochromator.

**Regioselective Chemistry.** Chemists embraced infrared lasers in the hope that "mode-selective" chemistry would be achieved by tuning the laser to a specific vibrational frequency, thus inducing reaction at a specific site within the molecule, locally associated with the vibration [6–9] This goal has not been achieved, owing to several factors: (i) prevalently used CO\textsubscript{2} lasers (10 μm) tend to excite skeletal modes that couple all atoms in a molecule, (ii) the multiphoton excitation process can itself deposit energy in many regions of the molecule, and (iii) intramolecular energy relaxation rates are generally fast compared to reaction rates and nanosecond laser pulse durations.

Point (i) can be addressed by exciting localized vibrational modes. C–H stretches in hydrocarbons are good candidates as they are associated with specific molecular environments [10, 11]. Point (ii) can be addressed by using molecules in which localized groups of states participate in the multiphoton process, leading to regiospecific (as opposed to bond- or mode-specific) excitation. This has been suggested in calculations by Marcus [12–14], and there are conflicting experimental results using chemical activation techniques [15–18].

Point (iii) was recognized by Rabinovitch [19–21]. Initially, local excitation leads to local reactions, in competition with intramolecular energy relaxation that produces an energy distribution equipartitioned over all internal degrees of freedom. If energy relaxation is fast compared to reaction, then the product distribution will be dominated by reactions of the thermalized (nonlocal) distribution. Products of the selective nonthermal reactions can be favored by collisionally quenching the slow reactions. When the collisional quenching rate is comparable to the internal energy relaxation rate, local selectivity can be observed.
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This has been observed in chemical activation systems, but never in an IRMPE experiment using nanosecond laser pulses, because collisions generally quench the IRMPE process at rates much lower than needed to observe localized reactions. Pulse lengths comparable to the energy relaxation time should prevent collisional quenching of the excitation process.

One candidate for regioselective experiments is a heavy atom–based molecule as suggested by Marcus. \((\text{CD}_3)_2\text{Sn}(i-\text{C}_3\text{H}_7)(i-\text{C}_3\text{D}_7)\) has been synthesized, and only the \(i\text{-C}_3\text{H}_7\) ligand will absorb in the C–H stretch region around 3000 cm\(^{-1}\). If excitation remains localized in the \(i\text{-C}_3\text{H}_7\) group, reaction may occur preferentially at that ligand to produce mainly H-containing products. If energy randomization occurs, then both H- and D-labeled products will be detected.

Another exciting possibility is to combine regioselective excitation of molecules by the IRFEL with VUV photodissociation. VUV photons from the ALS could be synchronized or delayed by several picoseconds to optimize the possible regioselective photochemistry.

3.2.2 Photodissociation Dynamics

High-energy photodissociation is important in astrophysical and atmospheric (pollutant) contexts and, like VUV spectroscopy, has been a subject of exploding interest. Among the many reasons for this heightened interest is the rich short-time dynamics of competing fragmentation channels that become available at energies two or three times that of typical chemical bonds. With active pump-probe synchrotron methods, we can determine branching cross sections for photodissociation into specific product states (in many cases highly excited radicals). This is most easily accomplished for emissive products. Indeed, photofragment fluorescence excitation spectra obtained at synchrotron radiation sources are a well-established source of information on the photodissociation dynamics of polyatomic molecules above ionization thresholds [22].

With the intensity of the ALS and probe-laser synchronization, it will be possible to carry such experiments a step further by actively interrogating the nature and reactivity of these product states, using the methods of laser-induced fluorescence and resonant multiphoton ionization. In such experiments, conducted at the CDRL, spectra of relative excitation cross sections for scattering into specific product states will be obtained by fixing the synchronized probe laser on individual product-state transitions and scanning the frequency of the synchrotron radiation. Branching at any particular VUV excitation energy will be found by scanning the
probe over the complete set of product-state transitions or by resolving the spectra of emissive products, in the normal fashion of studies of photodissociation dynamics [23]. In many cases, it will be useful to follow up ALS experiments with higher-resolution experiments employing transform-limited VUV laser radiation and with state-selected multiresonant multiphoton excitation techniques.

The ALS should also extend the possibilities of bond-selective chemistry in the UV. In the photodissociation of CH$_2$IBr, for example, it has been shown possible to selectively dissociate the stronger C–Br bond and keep the weaker C–I intact, by exciting the nonbonding electrons of bromine to an antibonding orbital of the C–Br bond. It will be very interesting to find whether a trend can be established by breaking the C–Cl bond in CH$_2$BrCl in an analogous way. This excitation will require wavelengths much shorter than 2000 Å. This study can be carried out with the ALS undulator beamline at low resolution, used essentially as a cw source, without the monochromator. To ensure sufficient signal-to-noise, cross-correlation modulation can be employed, using a beam chopper to modulate the photons from the beamline.

Along the line of high-energy excitation, the IRFEL is a potentially powerful preparative tool for exploring unique regions of 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 [24]. Using the IRFEL could extend this approach, which to date has been restricted to the excitation of 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 illuminate unique aspects of dissociation dynamics.

3.2.3 Rates of Rapid Reactions of Transient Organometallic Intermediates

During the past 20 years, the field of organometallic chemistry and transition metal catalysis has developed from an empirical, mostly synthetic endeavor to one in which attention is increasingly being paid to reaction mechanisms. Often these mechanisms involve the generation of very reactive, short-lived intermediates containing metals with open coordination sites, and their subsequent reaction with
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organic molecules. Most of our current information about these reactive organometallic species has been obtained from indirect studies, such as solution kinetics, tracer studies, stereochemical investigations, and isotope-effect studies. They have seldom been detected directly, and thus little is known about the absolute rates or the energetics of their reactions.

With the advent of techniques for measuring the rates of rapid reactions in condensed phases, this situation is now changing, and recently, flash kinetic studies of transient organometallic intermediates have begun to appear in the literature. Most of the early work in this area has been carried out on simple combination processes, such as the reaction of coordinatively unsaturated metal carbonyl complexes with dative ligands (e.g., phosphines or carbon monoxide). However, the most interesting and important organometallic reactions are processes in which transition metals induce bond cleavage and/or formation in organic molecules. Such processes are important in well-known homogeneous catalytic processes, such as hydroformylation, the Fischer-Tropsch process for conversion of CO and H₂ into alkanes and alcohols, Ziegler-Natta polymerization, and olefin metathesis.

Several years ago, a group led by Robert Bergman at LBL discovered a reaction in which certain complexes of iridium and rhodium undergo insertion (oxidative addition) into the C–H bonds of simple alkanes. Since discovery of the C–H activation reaction, an extensive series of indirect experiments have been carried out that have provided preliminary information about its mechanism. More recently, a flash kinetics system has been used to study fast C–H activation reactions directly. In preliminary experiments, this has been done by monitoring, in the IR spectrum near 2000 cm⁻¹, the reactions of one of the critical C–H activating intermediates, a cyclopentadienylRhodium carbonyl complex whose formula is (η⁵-C₅Me₅RhCO. This species has been generated using a XeCl excimer laser, and the rates of its rapid C–H insertion reactions have been monitored with a CO laser.

Although this has provided intriguing preliminary results, conclusive results have been precluded by the low resolution available with the CO laser, by its limited frequency range, and by the limited time resolution of the detector systems in use. The availability of the laser systems planned for the CDRL—especially the IRFEL—would greatly facilitate this research. It would widen the range of IR frequencies available, providing a means to monitor all the products of a C–H activation reaction, rather than just the few that absorb in a limited range accessible to the CO laser. In addition, by increasing the time resolution of the flash kinetics experiments, it would provide a way to examine C–H activation reactions that occur in the nanosecond-to-picosecond range. The IRFEL will permit threshold photodissociation of organometallics via IRMPD. Experiments in which carbonyls
are excited in the 5- to 6-μm range will be particularly valuable. The IRFEL combined with an ALS bending-magnet or undulator VUV probe opens the possibility of many new kinds of experiments. The frequency range, as well as the high intensity of the synchrotron light source, should allow researchers to move beyond their current focus on C–H activating intermediates that contain CO ligands, which will make accessible information about the dependence of reaction rates on the ligands attached to the metal center.

Because intermediates similar to those involved in C–H activation are also generated in other organometallic processes, the CDRL has the potential not only to advance our understanding of C–H activation reactions, but also to make important contributions across the broad range of organometallic chemistry.

3.2.4 Femtosecond Studies of Molecular Processes in Combustion

Rapidly advancing technology for generating ultrashort light pulses now provides the unprecedented opportunity to actually follow the internuclear motions of molecules in real time. Many important chemical processes, such as intramolecular vibrational energy redistribution, involve very rapid conversion of motion along one internuclear coordinate into motions in other directions. In many bimolecular reactions, motion along the collision coordinate must be rapidly converted into intramolecular motions to allow the formation of collision complexes. These processes are described by the time evolution of initially localized wave packets composed of superpositions of eigenstates of the system. Femtosecond laser pulses can create such localized excitations and then be used to probe their time evolution. Current measurements on dye molecules in solution are illustrative. In these experiments, an initial wave packet is generated by electronic excitation, and its subsequent motion affects the measured absorption of the sample. The sample’s transient absorption displays oscillatory components corresponding to vibrational motions of the excited molecules.

To extend these experiments to isolated gas-phase molecules and to make other classes of experiments possible, a femtosecond laser with greatly enhanced capabilities will be part of the proposed facilities at the CRF. This femtosecond laser system will provide an effective means for studying a variety of ultrafast molecular processes. One of the first applications will be to study the transient response of molecules in electronically excited states to learn more about the coupling of molecular motions in these states and to develop general insight into energy redistribution processes. Probing of dissociative electronic states gives the
opportunity to follow the course of a chemical reaction and observe the dynamical processes occurring during its course. The vibrational dynamics of highly excited molecules in the ground electronic state are of great interest, because most chemical reactions occur in the ground state. The capabilities of the CRF laser system, combined with techniques such as stimulated emission pumping, will make it possible to produce a large population of coherently excited molecules in the ground electronic state and to investigate vibrational energy redistribution on the ground potential surface. Some descriptions of specific experimental approaches to these studies follow.

(i) Gas-phase studies analogous to transient-absorption measurements in liquids are attractive, because the transient-absorption technique can be used to study any molecule that the laser can optically excite. When identical pump and probe wavelengths are used, these experiments are sensitive to motion of a wave packet away from its initial position; with continuum probes, the evolution of the excitation can also be followed. A tunable femtosecond laser able to provide 100-μJ pulses in the UV can excite a significant fraction of the molecules in a gas-phase sample and, in combination with sensitive absorption measurement techniques currently under development, will make a variety of transient-absorption experiments possible. For example, measuring the time-resolved absorption of molecules undergoing geometry changes following excitation will provide information on the fate of vibrational motions initiated by the excitation.

(ii) The femtosecond laser will be used in many ways to study the process of molecular dissociation. Time-resolved absorption of the dissociating molecule can be used to follow the dissociation path and reveal the involvement of motions off the reaction coordinate, perhaps showing when vibrational excitation of the fragments occurs. Combining femtosecond laser excitation with the photofragment-imaging technique developed at the CRF will allow additional, detailed information to be obtained about photofragmentation processes. Using a femtosecond pulse to dissociate a molecule and another femtosecond pulse to ionize the fragments will enable the correlation between dissociation time and the final fragment velocities to be measured. Because a fragment's velocity and its internal excitation are related, this technique can measure the time dependence of the dissociation into individual fragment states.

(iii) Intramolecular vibrational energy redistribution on the ground electronic potential surface plays an important role in unimolecular decay and in the formation and decay of collision complexes. Synchronization of a high-pulse-energy laser (such as the pump laser for the amplifier system) with the femtosecond laser will provide a unique possibility for exciting specific motions in molecules in
the ground electronic state. The high-pulse-energy laser can provide a large population of electronically excited molecules, from which high vibrational levels of the ground state can be reached by stimulated emission pumping with a femtosecond pulse. A second femtosecond pulse will then probe the decay of the vibrational wave packet by observing transient absorption or laser-induced fluorescence. Tuning the probe wavelength will be used to follow the evolution of the excitation. The stimulated emission pumping technique with nanosecond laser pulses has been applied previously to a number of interesting molecules, including acetylene, formaldehyde, and glyoxal.

3.2.5 Experimental Equipment

Apart from the facilities described in Section 5, the hardware requirements for the experiments outlined here include a set of conventional lasers and several vacuum chambers of varying sophistication. A number of the experiments require only a relatively modest vacuum chamber comprising 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 ports for the conventional lasers, the transform-limited tunable 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 such apparatus should be available so that one experiment can be prepared while a second one is under way. It is likely that many features of this modular apparatus will be similar to those required by other types of experiments, and every effort should be made 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.

For the purposes of molecular dynamics and dissociation experiments, a more elaborate experimental station for crossed-molecular-beam scattering studies and for acquiring angular distributions in photodissociation measurements is also required. This apparatus will be significantly more expensive than the modular apparatus and will require more sophisticated maintenance and oversight. The two choices for such an apparatus are a fixed-source chamber with a rotating detector and a rotating-source chamber with a fixed detector. The rotating-detector configuration offers great flexibility regarding the sources, as they are relatively unconstrained by size and pumping requirements, but it is limited by the difficulty, or even impracticality, of introducing light into the detector for optical detection. The
rotating-source configuration, on the other hand, provides great versatility in
detection, since the detector is fixed, but less flexibility in terms of the sources. The
ideal course of action would be to provide a machine of each type. These devices
would be used for some of the most elaborate experiments proposed for the CDRL.

Conventional lasers are also essential to doing interesting science at the
CDRL. Synchronization of the picosecond laser to the ALS and IRFEL is an
especially compelling need for the purposes of molecular dynamics research. The
near-transform-limited tunable UV laser is another capability that, because of its cost
and complexity, will be available to many workers only at the CDRL. The versatile
femtosecond laser system at the CRF falls in the same category. All three of these
laser systems are described in Section 5. More-routine types of lasers that offer the
capabilities needed for molecular dynamics studies include (i) excimer lasers for
photolysis, probably one operating on fluorine and one on chlorine, (ii) a CO₂ laser,
(iii) a frequency-doubled, excimer laser-pumped dye laser, (iv) a pair of frequency­
doubled dye lasers, pumped by an injection-seeded Nd:YAG laser synchronized to
the IRFEL macropulses, and (v) a continuous-ring dye laser for use with, among
other things, the ALS operating as a quasi-continuous source.

References: Intramolecular Dynamics and Primary Dissociation Processes

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3. RESEARCH OPPORTUNITIES

3.3 CLUSTER AND IONIC BEAM PROCESSES

The study of clusters is one of the most active areas in modern chemical physics [1]. Perhaps the principal fuel for this exploding interest is the desire to understand the physical and chemical properties of this new form of matter at a fundamental level. Of equal importance, however, is the hope and expectation that an understanding of clusters will solve some long-standing problems in catalysis and combustion, and that it may lead to dramatic discoveries regarding the microelectronic properties of materials. It is this synergistic combination of the fundamental and the practical that makes research in this area so exciting.

The following pages highlight three major areas of cluster research: spectroscopy, energetics, and dynamics. Since the work to be outlined involves ionic systems almost exclusively, research using ionic beams of smaller species will also be described. There are tremendous advantages in studying ions, because they can be easily transported, mass selected, stored in traps, and detected. Many of the proposed studies will give information directly on conjugate neutral systems, and for many properties, such as cluster binding energies and cluster reactivity, ionic and neutral systems give essentially the same results.

3.3.1 Spectroscopy

The IRMPE technique discussed in Section 3.2 is equally applicable to studies of species at low concentrations. The low densities of clusters [2, 3] and ions [4, 5] make spectroscopic characterization difficult, since the absolute absorptivity is very low. However, medium-size or large molecules will be in the region of the quasicontinuum after the absorption of one IR photon, and the wavelength dependence of IRMPD generally mimics the IR absorption spectrum of these molecules. By using the dissociation spectrum as a measure of the absorption spectrum, the inherent sensitivity enhancement afforded by particle detectors is obtained. The dissociation spectrum of clusters, ions, and solvated ions, therefore, practically provides an absorption spectrum that is otherwise unobtainable. Two-frequency experiments that use the IRFEL for the first one or two photons and a CO₂ laser for dissociation will be a powerful scheme that should improve both frequency resolution and yield. The pulse train from the IRFEL can be arranged such that the FEL macropulses will exactly couple to pulses from the CO₂ laser.

The following paragraphs expand on the use of the IRMPE technique with small clusters, as well as describing the IRFEL's uniqueness as a light source for
probing transition states and for obtaining far-IR spectra of radicals and radical clusters.

**Spectroscopy of Clusters.** Despite the strong current interest in clusters, 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 to measuring the vibrational spectra of a wide range of cluster species. The general method of investigation might be depicted as follows:

\[
\begin{align*}
M_n^+ & \quad \xrightarrow{hv} \quad (M_n^+)^* & \quad \xrightarrow{n\text{hv}} \quad \text{Products} \\
\text{IRFEL} & \quad \text{(scan)} & \quad \text{IRFEL} & \quad \text{CO}_2 \text{ Laser} \\
& & \quad \text{YAG Laser} & \quad \text{ALS}
\end{align*}
\]

When the first photon strikes a resonance, absorption of additional IRFEL photons is greatly enhanced, leading to product fragmentation; detection of fragments establishes the presence of a resonance. Other photon sources might also be used to enhance detection, as required.

In the reaction illustrated above, the symbol \(M_n^+\) symbolizes any of the species one might wish to investigate: (i) carbon clusters, including \(C_n^+, C_n^-, C_nO_m^\pm, C_nH_m^\pm\), etc., an understanding of which could have important consequences for modeling sooting flames [6–8]; (ii) metal clusters, including oxides, carbides, nitrides, etc. [9]; (iii) semiconductors; (iv) mixed metals or semiconductors; (v) alkali halides; (vi) physi- or chemisorbed adducts on clusters; or (vii) reaction intermediates. The emphasis initially will be on smaller systems \((n < 20)\), but there is no intrinsic reason larger systems could not be studied. As described below, both ion beam and ion trap instruments will be used, each having its particular advantages.

Perhaps the most important and interesting of the above systems are the various carbon and carbonaceous clusters, because of their potential importance in combustion processes. Also of practical interest are the physi- and chemisorbed adducts, as these systems should reveal a great deal about the catalytic properties of small metallic particles.

Neutral clusters can be studied using the same general methods. In this case, the products must to be detected via ionization, using either an \(F_2\) excimer laser or,
preferably, the ALS. Great care will have to be taken to ensure that the products come from the cluster of interest and not from larger clusters, since the neutral beam will not be mass selected.

Quantum Size Effects in Small Metal Particles. A great deal of effort is currently devoted to elucidating "quantum size effects" in small (10–100Å) metal particles. In particular, theoretical calculations have predicted quantum oscillations in the absorption cross sections from 50 to 300 cm$^{-1}$, which result from residual discreteness in the energy level distribution of the small particles. The only experiments on such systems have been performed in highly perturbing environments and have involved broad size distributions of particles. These effects have washed out the quantum structures predicted by theory.

It has been proposed that the far-IR characteristics of the IRFEL facility be used to carry out a detailed study of the 200- to 400-cm$^{-1}$ fine structure that has been tentatively observed in small metal particles. There are no alternative radiation sources available in this frequency region that are suitable for high-sensitivity, high-resolution measurements. Metal clusters will be generated by laser vaporization into a supersonic expansion. From the results of these studies it should be possible to address the nature and origin of quantum oscillations in metal particles in a meaningful way.

3.3.2 Cluster Energetics

Studies in this area are already enriching our fundamental understanding of how matter interacts and are serving to bridge the gap between our understanding of the gas-phase properties of atoms and molecules and the very different worlds of aerosols, liquids, and solids. Of additional interest here are how fundamental studies of cluster properties can help us better understand important practical processes like combustion and catalysis. Several types of experiments can be envisioned.

Measurement of Ionization Potentials.

\[
M_n (\text{or } M_n^+) \xrightarrow{\text{hv}} \text{ALS (scan)} \rightarrow M_n^+ (\text{or } M_n^{2+}) + e^- 
\]
In this experiment, a beam of neutral clusters or mass-selected ions is ionized using the ALS. Several methods can then 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 [10]. In the second, the photoion and photoelectron products are determined in coincidence as the ALS is scanned [11]. Again a threshold is determined. Finally, the ALS can be set at an energy above threshold and the energy of the photoemitted electrons can be analyzed. Each method has its strengths and weaknesses. In all of them, “cold” clusters are required and great care must be taken to eliminate hot-band contributions. The instruments required will be either a neutral/ion-beam apparatus or a time-of-flight analyzer, or a hybrid of the two. The ionization potentials that could be thus determined are extremely important for characterizing the structure and stability of cluster systems.

**Determination of Bond Energies.**

\[
M_n^+ \xrightarrow{hv, \text{ALS (pulsed)}} (M_n^+)^* \xrightarrow{\tau} \text{Products}
\]

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 \( \tau \) 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 [12]. These determinations can be done at several photon energies to ensure that consistent results are obtained. The ALS is essential for such experiments on larger clusters, owing to the large kinetic shifts in these systems and the requirement that the fragmentation take place on a microsecond time scale.

At present the primary method for obtaining thermochemical data of this kind is the measurement of endoergic energy thresholds by collision-induced decomposition. This is a useful method for small clusters, but many factors, especially the kinetic shift, rule out 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 yields the bond dissociation
energies for the neutral clusters. The method described here is, in fact, the only way these important neutral binding energies can be determined.

**Determining Lowest-Energy Pathways.** When energized particles dissociate, a number of reaction products are often 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,

\[
(C_{28}^+)^* \rightarrow \begin{array}{l}
C_{25}^+ + C_3 \\
C_{23}^+ + C_5 \\
C_{18}^+ + C_{10} \\
C_{14}^+ + C_{14}
\end{array}
\]

Here, energized \( C_{28}^+ \) undergoes metastable loss of \( C_3, C_5, C_{10}, \) and \( C_{14} \), all with significant intensities on the 10- to 30-\( \mu \)s 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:

\[
C_{28}^+ \text{ (cold)} \xrightarrow{\text{nhv}} \text{Products}
\]

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 other systems of interest.

### 3.3.3 Reaction Dynamics

A wide range of reaction dynamics studies can be envisioned, using the unique facilities of the CDRL. Brief summaries of only a few experiments are given below.
Studies of Reaction Complexes. One of the most important organic chemistry reaction mechanisms is the SN$_2$ mechanism. An example of such a reaction is

\[
\text{Cl}^- + \text{CH}_3\text{Br} \rightleftharpoons \text{Cl}^-\text{CH}_3\text{Br}
\]

\[
\downarrow
\]

\[
(\text{ClCH}_3\text{Br})^-* \rightarrow \text{ClCH}_3\text{Br}^- \rightleftharpoons \text{Br}^- + \text{CH}_3\text{Cl}
\]

The electrostatically bound cluster Cl$^-$·CH$_3$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 above. The rate-limiting transition state for the overall reaction is the quasi-symmetrical species (ClCH$_3$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 is also possible:

\[
\text{Cl}^-\text{CH}_3\text{Br} \xrightarrow{\text{IRFEL}} (\text{ClCH}_3\text{Br})^-*
\]

\[
(\text{ClCH}_3\text{Br})^-* \xrightarrow{\text{hv}} \text{Picosecond (delay)} \begin{cases} \text{Cl} + \text{CH}_3\text{Br} + e^- \\ \text{Br} + \text{CH}_3\text{Cl} + e^- \end{cases}
\]

The observed photoelectron spectrum should be strongly dependent on the delay time for the second photon, since the character of the initial photoexcited intermediate, (ClCH$_3$Br)$^-*$, will be changing rapidly 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 investigation will also be possible. During the last three years, it has been shown that photoelectron spectroscopy of negative ions can be used as a spectroscopic probe of the transition state region in neutral bimolecular reactions. Several hydrogen transfer reactions of the type A + HB $\rightarrow$ HA + B have been studied via photoelectron spectroscopy of the stable, hydrogen-bonded negative ions.
ion AHB⁻. This work has revealed previously unsuspected vibrational structure associated with the unstable [AHB] complex and has led to new insights into the microscopic, interatomic forces that govern the course of a chemical reaction. Much of the work to date has focused on reactions in which A and B are halogen atoms. It is now possible to investigate more complex reactions, particularly hydrogen abstraction reactions of the OH radical, such as OH + CH₃OH → H₂O + CH₃O. These reactions play a major role in combustion. The detailed information that will result from transition state spectroscopy experiments will nicely complement kinetics studies on these same reactions.

In one proposed experiment, the photoelectron spectrum would be measured for ions vibrationally excited with the IRFEL. This will allow one (i) to probe regions of the A + HB potential energy surface that are inaccessible via photodetachment of ground state ions and (ii) to control the decay paths of the unstable [AHB] complex. As with earlier work on ground state anions, the initial experiments will focus on triatomic systems. Consider the reaction Br + HI → HBr + I, which can be studied by photodetaching BrHI⁻. To first order, the structure of the ion is BrH·I, and photodetachment of the ground state ion primarily accesses the I + HBr product valley on the neutral potential energy surface. However, a single quantum of excitation in the v₃ mode of the ion at 920 cm⁻¹ (the “antisymmetric” stretch) results in substantially greater overlap with the barrier region and reactant valley on the Br + HI surface, thereby allowing one to probe this chemically important part of the surface with this experiment. In addition, while photodetachment of ground state BrHI⁻ populates levels of the [BrHI] complex that decay almost exclusively to I + HBr, photodetachment of vibrationally excited BrHI⁻ results in substantial population of [BrHI] levels that decay preferentially to the Br + HI channel, which lies 0.75 eV above the I + HBr channel. Hence, a small amount of vibrational excitation in the ion can drastically increase the yield of an energetically unfavorable neutral product.

The IRFEL is an ideal light source for this experiment. The experiment requires pumping a large (>10%) fraction of the ion population to the v₃ = 1 state, and the FEL is the only source with sufficient power in this frequency range to do this. An important consideration is that several rotational levels of the ion are populated, even though the ions are rotationally cold. The relatively broad bandwidth of the FEL is actually an advantage in this case, as it should allow simultaneous saturation of several vibration-rotation transitions, thereby increasing the fraction of ions in the upper vibrational state.

The initial work on the Br + HI reaction might then be followed by studies of hydrogen transfer reactions that are important in combustion. These include the
hydrogen abstraction reactions of the OH radical alluded to previously. There is also interest in reactions of O₂ with hydrocarbon radicals. For example, the reaction C₂H₃ + O₂ → C₂H₂ + HO₂ represents a major pathway for the vinyl radical formed in ethylene combustion. In these studies, the appropriate hydrogen-bonded anion will be vibrationally excited with the IRFEL, followed by photodetachment with a pulsed laser and measurement of the electron kinetic energy distribution. By exciting different vibrational modes of the anion, one should be able to map out the transition state region for the neutral reaction. This information, in conjunction with theoretical studies on polyatomic reaction dynamics planned for the CDRL, will enhance our understanding of how the distribution of reactant energy affects the overall properties of these reactions.

Investigation of Isomerization Barriers. An example of an experiment to determine an isomerization barrier was given above. A second, much different example is the following:

When vanadium ion is clustered to water, two forms are possible: the "electrostatic" complex V⁺·H₂O, 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 with 100% purity in a jet expansion. This complex can be irradiated by the IRFEL and the photofragment spectrum monitored. The onset of the HVOH⁺ spectrum indicates that the photoexcited V⁺·H₂O complex has isomerized, and analysis will yield the isomerization barrier.

3.3.4 Experimental Equipment

At least three separate instruments will be required to perform all the experiments outlined above. Brief descriptions of these instruments follow,
together with a list of the conventional lasers that would be most useful for cluster and ion beam studies. It would also be useful to improve the resolution of the IRFEL; an IR interferometer might be developed for this purpose.

**Ion Beam Machine.** In this instrument, ionic clusters would be made either in continuous or pulsed jet expansion sources, mass selected by a quadrupole, and deflected into an octupole ion guide/trap, where they can interact with photons from the IRFEL, the ALS, or any of various conventional lasers. The clusters would then be deflected into another quadrupole mass filter and finally detected using single-ion-counting methods. This instrument would be used primarily in the determination of binding energies of clusters or ligated clusters and in vibrational spectroscopy of smaller cluster systems, where dissociative detection can occur on a sub-millisecond time scale. It would also be used for ionization potential measurements in which the detected particle is the product ion. For measurements of first ionization potentials, the cluster source would be aligned coaxially with the ALS, since a neutral cluster beam would be required and these beams cannot be deflected. The cluster ions can be detected off axis in the usual manner. For second ionization potentials, mass-selected cluster ion beams would be used, together with the configuration described first.

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

**ICR Ion Trap.** The envisioned ion-cyclotron-resonance (ICR) ion trap would use a pulsed laser–desorption cluster ion source for external injection into an ion trap enclosed by a 7- to 10-tesla superconducting magnet. Ion detection, ejection, and energizing would be accomplished by state-of-the-art fast Fourier transform electronics and an associated computer system. Provision would be made initially
to cool the ICR cell and vacuum system to 77 K, with eventual cooling to 4 K. This instrument is essential for much of the vibrational spectroscopy and for the lowest-energy-pathway experiments. This device could also be used to "chemically" prepare certain clusters in situ, which could then be interrogated using the IRFEL, the ALS, or both. Conversely, photochemistry in the ion trap could be used to prepare exotic ions whose chemistry would then be probed.

Conventional Laboratory Lasers. All of the experiments described above will utilize either the IRFEL or the ALS, or both. In most cases, additional conventional lasers will also be required to generate the ions, to allow double resonance experiments, or to assist in detection. Those lasers required for the work outlined here include (i) a 1000-Hz excimer laser for cw cluster generation, (ii) a high-rep-rate Q-switched YAG/dye laser for photofragment spectroscopy, photoelectron spectroscopy, and pulsed cluster generation, (iii) a high-power pulsed CO$_2$ laser for multiphoton dissociation, and (iv) an F$_2$ excimer laser for product ionization. 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.

References: Cluster and Ionic Beam Processes


3.4 SPECTROSCOPY, ENERGETICS, AND DYNAMICS OF FREE RADICALS

Emerging as an area of particular importance is the direct detection of transient free radicals relevant to combustion, high-technology manufacturing, the environment, and hydrocarbon processing. Reactive free radicals are often the active species controlling complex chemical reaction networks, yet they are the most difficult to understand because of the difficulty of studying them. It is difficult to produce many radicals by conventional photochemical methods without an appropriate synthetic route to a suitable photochemical precursor. However, infrared multiple-photon dissociation (see Section 3.2) provides a general route to many molecules by inducing thermal dissociation of an appropriate simple hydrocarbon precursor. Our knowledge of hydrocarbon thermal chemistry provides guidance for the initial bond-breaking sequence many molecules will undergo when heated rapidly (as by a pulsed IR laser). The following radicals have been formed from the precursors indicated using tunable 3-μm radiation from an optical parametric oscillator:

<table>
<thead>
<tr>
<th>Radical</th>
<th>Precursor</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃</td>
<td>C₂H₆, C₃H₈, C₄H₁₀</td>
</tr>
<tr>
<td>C₂H₅</td>
<td>C₂H₆, C₃H₈, C₄H₁₀</td>
</tr>
<tr>
<td>C₃H₇</td>
<td>C₄H₁₀</td>
</tr>
<tr>
<td>C₂H₃</td>
<td>C₃H₆, 1,3-C₄H₆</td>
</tr>
<tr>
<td>C₃H₅</td>
<td>C₃H₆, C₄H₈</td>
</tr>
<tr>
<td>C₃H₃</td>
<td>1,2-C₄H₆</td>
</tr>
</tbody>
</table>
Sufficient quantities of radicals can be formed as primary dissociation products for spectroscopic measurements (for example, photoionization or laser-induced fluorescence), as well as photodissociation investigation (see the discussion of the feasibility of IRMPE with the IRFEL in Section 3.2). An inherent advantage of pulsed laser production of radicals is the ability to probe (with a second pulsed laser) on a time scale faster than recombination [1]. Conventional thermal or pyrolytic reactors with residence times of 1–100 ms often have low radical concentrations owing to recombination in the reactor. Probing with a pulsed laser following pulsed generation of the species of interest yields higher transient concentrations and consequently better sensitivity. An extension of the spectroscopic diagnostics using two pulsed lasers is that kinetics can be directly followed in time by varying the time delay between the excitation and detection pulses.

3.4.1 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 the 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 these potentials are often poorly known. Infrared absorption spectroscopy of gas-phase radicals is still poorly developed, owing to the difficulties of creating a sufficient number-density of radicals, detecting the absorption spectrum, and identifying the spectral carrier. Infrared absorption spectra, even at a resolution of 2–5 cm\(^{-1}\), 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. For these purposes, 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 IR region (\(\omega_{IR}\)) and the other in the VUV (\(\omega_{UV}\)), 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 [2] have recently demonstrated a continuous pyrolysis source of vinyl and ethynyl radicals, producing number-densities of \(10^{14}\) cm\(^{-3}\) at the nozzle and \(>10^{10}\) cm\(^{-3}\) in a skimmed beam 30 cm downstream.
First, the photoion yield curves (mass-selected parent or fragment cation current vs $\omega_{UV}$) of the free radicals will be measured by crossing a VUV photon beam at 7–11 eV (from 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 $\omega_{UV}$ can provide cation vibrational spectra as well.

Next, survey IR absorption spectra with 2–5 cm$^{-1}$ resolution will be obtained using the IR + UV R2PI technique, with $\omega_{IR}$ scanned and $\omega_{UV}$ fixed. The IRFEL provides $\omega_{IR}$, and the laboratory laser system provides $\omega_{UV}$; the pulse structure of these systems are well-matched. Mass-selected cation yield vs $\omega_{IR}$ constitutes the IR absorption spectrum. One can expect $10^4$–$10^5$ cations per second in this mode. Judicious choice of $\omega_{UV}$ and of the cation detected will maximize discrimination between $v = 0$ and $v = 1$ radicals and will minimize background signals.

There are now two ways to proceed. One can use the parent cation yield curve to set $\omega_{UV}$ 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 for polyatomic radicals) and if the Franck-Condon factor $\left| \langle v = 1 \mid v^+ = 0 \rangle \right|^2$ is sufficiently large. The technique will be most sensitive to those radical vibrations that carry the radical geometry toward the cation geometry. Alternatively, one can use a fragment cation as detector and set $\omega_{UV}$ 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 ($\sim 10^{-3}$ cm$^{-1}$ resolution), one can combine a cw F-center laser ($\sim 10$ mW in the IR) with the ALS, using the latter as a quasi-cw VUV source. Signal estimates are $10^3$–$10^4$ cations per second in this mode.

In some cases, laboratory lasers alone have been used to obtain radical IR absorption spectra in certain wavelength regions. However, 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 the entire “chemical infrared,” from 200 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.
Survey spectra from the IRFEL will obviate the search problem inherent in high-resolution work.

The unique combination of the IRFEL, the ALS, and laboratory lasers will permit a comprehensive program in 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 IR-UV resonance ionization detection will be limited primarily by the experimenter's ingenuity in designing suitable 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.

3.4.2 Far-IR Absorption Spectroscopy of Radicals and Radical Clusters

The far-IR capability of the proposed IRFEL facility will be utilized to study low-frequency vibrational modes in fluxional free radicals and to investigate internal modes (hindered rotations, van der Waals vibrations) in weakly bound clusters of radicals. Emphasis will be placed on the development of suitable new technology for measuring high-resolution absorption spectra of such elusive transient molecules in spectral regions where no alternative spectral sources exist.

Many free radicals possess interesting large-amplitude internal dynamics that influence their reactive properties. For example, torsional motions in chain hydrocarbons (ethyl, n-propyl, etc.), large-amplitude bending motions in linear carbon chains, and hydrogen tunneling migration in other radicals (e.g., vinyl) are likely to occur at far-IR frequencies. Such species are extremely difficult to study at a level of detail that reveals these dynamical effects, even using the best modern techniques.

Spectroscopic studies of complexes of free radicals, bound by weak van der Waals forces, offer particularly interesting new insights into chemical reactions. For example, by studying the spectra of complexes of radicals formed with reaction partners (e.g., OH·CH₄), one can access the entrance channel regions of bimolecular reactions, probing both the potential surface itself and the dynamics that occur on it. Such studies will nicely complement the pioneering research of Neumark and coworkers on the transition states of bimolecular reactions and will elucidate the effects of long-range forces on the orientation dependence of chemical reactions. These complexes are most effectively studied at far-IR frequencies, thus directly sampling the internal motions (e.g., internal rotation of OH) within clusters.
It is convenient to define the far-IR as the region from where millimeter techniques begin to fail (10 cm\(^{-1}\) = 1000 \(\mu\)m) to frequencies where lead-salt diode laser technology becomes operative (350 \(cm^{-1}\) = 30 \(\mu\)m). Of this region, the portion from 10 to 100 \(cm^{-1}\) (1000–100 \(\mu\)m) is covered quite effectively by the technology of tunable far-IR laser spectroscopy. While there are good prospects for extending the high-frequency limit for this technology to about 150 \(cm^{-1}\), it will be more difficult to access shorter wavelengths. The proposed FEL facility is designed to operate down to frequencies of 200 \(cm^{-1}\) (50 \(\mu\)m), and possibly lower. Consequently, it will become the only coherent radiation source that can operate usefully for purposes of ultrasensitivity high-resolution absorption spectroscopy in the range <200–350 \(cm^{-1}\), offering several orders of magnitude higher sensitivity than achievable with state-of-the-art Fourier transform methods. By combining the IRFEL with new methods recently developed for producing and cooling radicals and their complexes in supersonic free jets, new classes of molecules and new classes of dynamical phenomena of importance in combustion science can be addressed with the full power of high-resolution spectroscopy.

One in-house laboratory proposed for the CDRL will specialize in the development of far-IR technology required for utilization of the IRFEL in this region. Several modern far-IR detector systems (stressed photoconductors, Schottky diodes) will be constructed and tested. Necessary optical components, including polarizers, interferometers, and frequency-measuring systems will be constructed. These devices and the associated expertise of the research group will be available to the general community, thus opening up a hitherto neglected portion of the spectrum for research.

3.4.3 Combustion Kinetics Studies

The multiple-beam Nd:YAG/dye laser system proposed for the CRF offers unique capabilities as a probe for laser photolysis-initiated reactions. The laser-photolysis/cw-laser-induced fluorescence (LIF) technique is an extremely precise means of measuring reaction-rate coefficients, but it is limited to the study of species that can be probed using cw dye-laser technology. The multiple-beam laser system will allow extension of this technique to the study of species not accessible with cw lasers. Instead of a cw probe of reactant concentration, equally spaced pulses from the multiple-beam laser will probe the concentration profile at discrete times during its decay. Time scales for radical decay in these experiments typically range from 100 \(\mu\)s to 10 ms, requiring an instantaneous laser repetition rate of 1 to 100 kHz, well
within the laser's specifications. Since the entire radical decay profile is discretely sampled with every photolysis pulse, the experiment will be insensitive to shot-to-shot fluctuations of the photolysis laser, yielding enhanced signal-to-noise relative to that in a typical pulsed-photolysis/pulsed-LIF experiment.

Particularly attractive is the use of the multiple-beam laser system for studying reactions of ground- and excited-state atomic species. The reactions of many important atoms are very poorly understood at present, owing in part to lack of sensitive spectroscopic probes. The high peak powers present in the multiple-beam laser pulse train will make possible a variety of less conventional spectroscopic probes that are well-suited to detecting atoms. Vacuum UV light can be generated and used for single-photon LIF, and UV light can be generated and used for two-photon LIF or three-photon ionization detection. Laser probes based on these techniques have already been demonstrated for a wide variety of atoms in both their ground and excited states, including H, C, N, O, S, F, Cl, and I; extensions to other atoms are straightforward.

As an example, reactions of the carbon atom can be studied in its ground, $2^3P$, state with O$_2$, NO, N$_2$O, H$_2$, etc. Reactions of carbon atoms are important in the conversion of NO to CN in rich hydrocarbon flames, a process important in determining the final amount of NO$_x$ that escapes a flame. There are only a few determinations of room-temperature carbon-atom reaction-rate coefficients, and no studies of their temperature dependences. Carbon atoms can be conveniently made by excimer-laser photolysis of C$_3$O$_2$, initiating the experiment. A train of pulses from the multiple-beam laser with an overall duration of 10 ms will be doubled to 308 nm for two-photon LIF on C($2^3P$). Measured LIF signals will be normalized with respect to probe-laser power, signal averaged, and analyzed to extract the pseudo-first-order rates. This data will be of much higher quality than that from the traditional pulsed-photolysis/pulsed-LIF technique, both because of the tenfold increase in signal and because of the inherent immunity to fluctuations in photolysis-laser power.

For reactions exhibiting single-exponential decays, the multiple-beam laser pulses will be equally spaced in time, spanning three or four $1/e$ lifetimes of the decay. Nonexponential decays are encountered in a variety of addition reactions. Measuring these decays accurately requires a high sampling rate at the beginning of the decay, with a much lower sampling rate required at long times. The multiple-beam laser system will be ideal in these situations, since its pulses need not be evenly spaced in time.
3. RESEARCH OPPORTUNITIES

3.4.4 Energetics and Dynamics of Free Radicals

For many weakly bound polyatomic radicals, the bond dissociation energies are as low as 10 to 30 kcal/mole. The tunable IRFEL is powerful enough to excite several quanta of the C–H stretching vibration and thus to induce dissociation. The dissociation lifetime of these weakly bound medium-size polyatomics is expected to change drastically. By operating the 10-ps IRFEL pulses synchronously with VUV output from the ALS, and by measuring the dissociation lifetime of excited molecules under various excitation conditions by time-delayed photoionization of the dissociation products, it will be possible to understand in detail not only the IRMPE process through high-frequency C–H stretching modes, but also the intramolecular dynamics that lead to dissociation.

The bond dissociation energy of free radicals can also be measured accurately by inducing dissociative ionization to determine the threshold energy for ion-pair production. For example, the electron affinity of CH₂=Cː can be measured with high precision by using the method of photodetachment of negative ions. If the electron affinity in known, the C–H bond dissociation energy of CH₂=CHː can be obtained with high precision by using radiation from the ALS to measure the threshold energy for the photochemical process CH₂=CHː → CH₂=Cː⁻ + H⁺.

An intense beam of CH₂=CHː can be produced by photodissociating CH₂=CHBr by multiple-photon dissociation using the IRFEL or by laser excitation.

3.4.5 Experimental Equipment

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 and a TOF photoelectron 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.

50
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.

References: Spectroscopy, Energetics, and Dynamics of Free Radicals


3.5 SURFACE AND CONDENSED-MATTER PROCESSES

Surfaces invariably play an important role in dynamical processes involved in the creation and destruction of pollutants, particulate formation, and other steps in the combustion cycle. It is crucial to develop advanced techniques for characterizing surfaces and interfaces and for monitoring the physics and chemistry of the pertinent processes. In particular, following the surface chemical dynamics of radicals and of molecular species such as hydrocarbons and CO can substantially enhance our understanding of combustion processes. In addition, studies of energy relaxation of molecules at surfaces will provide information on surface processes in catalysis.

Of the many different methods developed for probing surfaces and interfaces, optical techniques offer the advantages of being nondestructive and widely applicable. Accordingly, this section outlines a number of themes that might be pursued in exploiting the facilities of the CDF in studying processes at surfaces, as well as those in condensed phases.

3.5.1 State-to-State Chemical Dynamics at the Vacuum-Surface Interface

Chemical dynamics of molecules colliding with and reacting on the surfaces of solids is an area of vital importance in combustion, and the facilities of the CDRL
3. RESEARCH OPPORTUNITIES

will enable a new generation of experiments in this field. The goal in studies of surface chemical dynamics has always been to prepare molecules in known electronic, vibrational, and rotational states and to collide these, with a known kinetic energy, with a well-defined surface. Subsequent state-resolved analysis of the products would then complete the picture of a surface chemical reaction at a fundamental level. The combination of the IRFEL, the ALS, and visible lasers will allow this level of study to take place for the first time.

In virtually all state-to-state scattering studies to date, the initial state distribution has been 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 ever to be studied, 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 IR-active (e.g. H₂).

In addition to allowing control of the initial state that collides with the surface, the combination of the IRFEL and ALS 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 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 (Cₙ-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 the population in \( v'/ = n + 1 \).

The presence of a highly vibrationally excited beam of molecules will also 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 recently been shown to have atomically smooth surfaces (about one hundred lattice spacings) and to offer the added advantage of remaining clean under normal (10⁷ torr) vacuum conditions, thus not requiring the very low pressures (10¹¹ 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.

3.5.2 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, bond-making, and energy transfer processes on surfaces, and in some specific cases, to help understand important practical applications of photons in driving surface processes. 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? The IRFEL at Stanford has recently been used by George to study a surface predissociation reaction, the IR-induced desorption of butane from Al_2O_3. The high power and broad tunability of the FEL were essential. It was observed that butane desorbs via a one-photon IR adsorption when the FEL is resonant with a CH vibration (within the 15 cm^{-1} bandwidth). By doing isotopic substitutions and by co-adsorbing other molecules, it was also shown that absorption of the IR photon by a neighboring molecule can desorb a nontargeted molecule. Based on this precedent, one can say that the single- and multiple-photon-induced desorption of many different kinds of molecules from insulator, metal, and semiconductor surfaces can be explored at the CDRL.

In the gas phase, vibrationally excited molecules have been shown to predissociate weakly adsorbed adducts, such as noble gases. Thus, by analogy, a monolayer (or more) of an adsorbed molecule will be covered with a sub-monolayer of helium or neon, and the sample cooled to 4 K. The desorption of the rare gas, following absorption 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 will allow a rapid enough desorption rate that the internal states of the desorbed molecules can be determined by the advanced dye laser spectroscopy system to be available at the CDRL.

The CDRL can also be expected to play a role in the study of electronically, as well as vibrationally, excited molecules on surfaces. The primary goal of these studies will be to better understand surface photochemistry. The two primary processes of interest here are photodissociation of an electronically excited adsorbed species (the chemical reaction of interest) versus charge transfer to the substrate (which acts to quench the chemical reaction). A focus for the first experiments could
be to understand these processes when the species involved are chlorinated hydrocarbons, molecules of obvious technological, economic, and environmental importance. 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 (i) hot substrate photoelectron dissociative attachment to the adsorbate, (ii) valence excitations of the adsorbate to known internally repulsive states, (iii) hot hole chemistry, (iv) dipolar repulsive states, (v) core-hole-induced reactions, and so on. To explore any but the first two of these, tunable UV beyond 6 eV is required. The ALS will provide these photons. At $3 \times 10^{14}$ photons/s, at the tightest possible focus, a flux of $10^{19}$ photons/s-cm$^2$ is possible. Since the typical cross sections for photochemistry are about $10^{-19}$ cm$^2$, this implies that nearly full photolysis might be expected in times on the order of 1 second. The spectral dependence, as it correlates to the onset of allowed processes, should give immediate information on which of the processes are operative.

The femtosecond dynamics that leads to dissociation is typically in competition with charge transfer processes occurring 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 at the CDRL.

### 3.5.3 Spectroscopy and Dynamics at Interfaces by Nonlinear Optical Techniques

For optical studies of surface and interface systems, the IRFEL and the ALS provide, in many respects, clearly identifiable advantages over existing light sources. For example, a second-order nonlinear optical method has recently been developed for surface studies. It involves the detection of a coherent output at frequency $\omega_1 + \omega_2$ when two input laser beams at $\omega_1$ and $\omega_2$ are incident on a surface. The method is highly surface-specific by symmetry, and is applicable to all types of interfaces. It is becoming one of the most versatile probes in surface science. With tunable lasers as the pump source, this technique can also be used for surface spectroscopy. Infrared tunable lasers are particularly useful in this respect, as they will allow the study of
surface vibrational modes and hence selective detection of molecules at surfaces or interfaces. The technique is already well-developed, but it is currently hampered by the unavailability of widely tunable IR laser systems. The proposed IRFEL would be the major breakthrough that this technique needs, allowing any molecules and radicals of interest to be studied.

One proposed approach would rely on IR-visible sum-frequency generation (SFG) for surface studies, using a picosecond IRFEL as the IR pump source and a picosecond visible laser as the visible pump source. With the IR frequency tunable over the 3- to 50-μm region, most of the important vibrational modes can be probed. The technique can then be used for surface vibrational spectroscopy and for selective detection of adsorbed molecular species, as vibrational spectra are fingerprints of molecules. The possibility of studying spectroscopy of buried interfaces is most exciting, because few other techniques exist for such studies. With picosecond IR and visible pump pulses, the SFG technique can be used to study surface dynamics on the picosecond time scale. This will open a new research area with many exciting opportunities. Examples are studies of lifetimes and dephasing times of surface excitations, surface melting and phase transition dynamics, energy transfer, surface diffusion, and so on. State-specific, site-specific, and molecule-specific dynamic studies are possible via selective IR excitations, followed by SFG, CARS, or transient absorption detection.

Nonlinear optical techniques can also be used to study selective surface reactions on a picosecond time scale. To really understand a reaction, one must be able to follow the steps of the reaction; however, this is a difficult task with available techniques. With picosecond IR-visible SFG, it actually becomes possible to selectively detect a particular molecular species and follow its reaction path. The appearance and disappearance of an intermediate species in a reaction could also be monitored.

These techniques are not limited to gas-solid interactions. They are applicable to all types of interfaces, as long as they are accessible by light. Thus, a wide variety of material systems can be studied. Many of them are highly relevant to modern technology. These include surfactants on liquids and solids, membranes, metals and semiconductors in electrolytes, polymer/metal interfaces, ceramic/metal interfaces, insulators and semiconductors, and many others. There is no doubt that the technique will have a very bright future with the help of an IRFEL.

In addition, a new set of interesting problems at interfaces can be investigated with the combination of the IRFEL and the ALS. For these problems, the IRFEL will be used to excite or perturb the surface, and the synchrotron radiation will be used to
probe the excitation or perturbation and the ensuing relaxation. For example, desorption of adsorbates may be induced by mode-selective vibrational excitation by the IRFEL. Will desorption occur only for the molecules that are being excited or will thermalization of the photon energy desorb surface molecules indiscriminately? Crucial information regarding the desorption mechanism may be obtained using the IRFEL pump–ALS probe technique. Thermalization of surface adsorbates excited vibrationally and/or electronically may be studied. The IRFEL or a UV photon serves as the pump, and surface second-harmonic generation probes the thermalization rates. Bond-selective surface photochemistry induced by ALS excitation is an interesting possibility that should be pursued as well. Other possible projects are the investigation of induced surface-phase transformation, dynamics of surface states, two-dimensional carrier dynamics, surface impurity states, time-resolved molecular rearrangement, and so on.

3.5.4 Dynamical Processes in Solution

With the advent of picosecond and femtosecond laser sources, it has been possible to observe, in real time, the fundamental stages of a variety of chemical reactions in solution. Currently, experiments that probe vibrational dynamics on ultrafast time scales are not feasible, owing to the lack of high-power sources in the vibrational IR. The implementation of an IRFEL would open up entirely new classes of experiments in condensed-phase reaction dynamics.

The IRFEL, in combination with existing ultrafast lasers and the ALS VUV beamline would allow direct studies of vibrational energy flow in a molecule in solution. Experiments could be done to match intramolecular vibrational redistribution among modes of the molecules, or to observe the flow of vibrational energy during chemical bond formation or dissociation. A molecule can be photodissociated with a femtosecond laser source and the vibrational energy distribution of the fragments probed with the IRFEL pulses. Time-resolved vibrational information could thus be obtained. Such experiments would greatly enhance our understanding of how chemical reactions proceed in solution.

3.5.5 Hole-Burning Spectroscopy

The proposed combination of tunable, pulsed, IR, visible, and VUV photon sources at the CDRL will be invaluable 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 that typically exist in solids and clusters leads to inhomogeneous broadening of spectral lines. 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 that can be performed include the following: (i) A hole can be burned using a visible or UV pulse, and an IR probe then used to see the resulting change in nuclear configurations upon electronic excitation. (ii) 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. (iii) A hole in the vibrational spectrum can be burned using the IRFEL, and the effect of this on the electronic spectrum can be explored. (iv) Conventional hole-burning experiments, in which the pump and probe pulses are in the same frequency range, will be greatly facilitated, particularly by the IRFEL. Conventional laboratory sources do not have sufficient intensity for many applications. The following paragraphs expand upon these possibilities.

**Shape and Size Distributions in Finite Semiconductor Crystals.** Techniques have been developed for preparing finite-size crystals of many common semiconductors, and the intrinsic optical properties of this class of materials are currently being explored. 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 IR absorption frequency of these finite dielectric crystallites depends solely on the shape, not on the size of the crystals. Existing methods of preparation produce a distribution of cluster sizes and shapes, resulting in inhomogeneous broadening of the optical spectra. Combined IR-visible hole-burning experiments will allow the effects of size and shape variation on the optical spectra to be separated.

**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$_3$D$^+$ [1]. The burning leads to a disequilibrium in the crystals, followed by reequilibration. The kinetics of both the disequilibration and the reequilibration process are of interest. Currently, only very special crystals can be examined—and those only at low temperatures. 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
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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 IR 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 can exist in multiple conformations and thus offer another subject of study [2]. 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 catalysts are typically materials in which there are distributions of chemical environments. At present the spatial distribution of these environments 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 likely to be developed at the CDRL 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 that the molecules experience inside a catalyst will then be used to understand the mechanisms by which catalysis occurs.

3.5.6 Dynamic Optical Studies of Electronic States in Semiconductors

Our present understanding of dynamic properties of defects, such as multistep recombination processes of free carriers via bound excited states into the bound state of a defect, is far from satisfactory, because no studies have been performed in real time.

With the new facilities, it will be possible to perform dynamic, real-time studies of excitation and relaxation phenomena associated with defects in
semiconductors. Pump-probe-type experiments can be performed with an IRFEL, in combination with standard lasers. The study of the fundamental recombination processes in shallow, hydrogenic dopants (shallow acceptors and donors) would require photon energies in the range from 10 to 100 meV \( (80 \text{ cm}^{-1} < \nu < 800 \text{ cm}^{-1}; 120 \mu\text{m} > \lambda > 12 \mu\text{m}) \).

Direct measurements of temporal characteristics of excitation and recombination processes [3] would be permitted. The tunability and high intensity of the IRFEL will provide a unique opportunity to study transitions between s-like excited states of defects.

The energy transfer between modes of a given center and the lattice modes can be studied in real time with the IRFEL. The energies of most modes lie between 40 and 250 meV \( (320 \text{ and } 2000 \text{ cm}^{-1}, 30 \text{ and } 5 \mu\text{m}) \). The intense IR radiation source can also be used for selective excitation of local vibrational modes associated with the defects in semiconductor crystals. At a high enough excitation level, one could observe radiation-induced structural transitions, including dissociation of defect complexes or motion of impurities between nonequivalent local minima in the crystal lattice. This could not be done with weaker sources.

3.5.7 Experimental Equipment

Apart from the two apparatus described below, a low-temperature (liquid-helium) cryostat with optical interface and IR probe lasers of high stability and reasonably broad tunability will be needed for general use.

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 to be available at the CDRL, namely, the IRFEL, the ALS, and the advanced laser systems. This apparatus will combine, for the first time, a universal electron-impact-ionizer mass spectrometer detector with a photoionization TOF spectrometer and an opothermal detector.

All three detectors will be rotatable around a vertical axis. A fixed-mass spectrometer detector will also be present and will make use of the photons from the ALS as a source for ionization. The ion source of this detector will be cooled to liquid-helium temperature to take advantage of the much-reduced background pressure under such conditions. The electron-impact mass spectrometer will identify the products of a reaction and their velocities and angular distributions. The TOF photoionization mass spectrometer will identify the molecular vibrational
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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 helium diffraction measurements. The other feature of the apparatus are described below.

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

- Ultrahigh-vacuum scattering chamber. The scattering chamber should have a base pressure below $10^{-10}$ torr and should 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 three translational and three 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 that does 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 CDF, 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.

**Apparatus for Nonlinear Optics at Interfaces.** For the nonlinear optics experiments, a general purpose ultrahigh-vacuum chamber will be needed. This chamber will be provided with standard analytical tools (Auger, LEED, mass spectrometry, and ion sputtering) and a crystal manipulator that can be cooled to liquid-nitrogen temperatures.
In addition to the special laser facilities described in Section 5, a YAG-based laser (or a TiAl$_2$O$_3$-based system if available at that time), tunable in the visible and IR and with a kilohertz repetition rate, will be needed. A multichannel photon detection system will complete the equipment needed for this type of experiment.

References: Surface and Condensed-Matter Processes


3.6 **COMBUSTION DIAGNOSTICS**

Turbulent flames have spatial and temporal variations in properties such as species concentration, temperature, and velocity. Understanding the dynamics of these variations is a fundamental problem in turbulent flow research. These variations often occur on sub-millisecond time scales and on sub-millimeter length scales. Probe sampling of highly turbulent flows rarely resolves these variations in properties. Laser-based techniques are far more powerful in terms of temporal and spatial resolution than probe sampling techniques.

The proposed multiple-beam Nd:YAG/dye laser system offers important new capabilities for investigating turbulent reacting flows. The system will provide unique capabilities for point measurements, for fast-frame-rate digital imaging, and for three-dimensional imaging. The following paragraphs focus on proposed expanded capabilities for performing measurements in turbulent reacting flows. We briefly review how such measurements have improved our understanding of turbulent flames and then cite several important experiments that will become possible with the multiple-laser system. An experiment using the femtosecond laser system is also described.
3.6.1 Laser-Based Point Measurements in Turbulent Reacting Flows

The simultaneous multispecies capability of spontaneous vibrational Raman scattering is ideally suited for investigations of turbulent jet diffusion flames, where a jet of fuel issues into stagnant or coflowing air [1]. The Raman technique allows one to measure on a spatially and temporally resolved basis the extent of fuel-air mixing and, to a limited extent, the progress of the chemical system toward equilibrium. Because the chemical kinetics are very fast, the hydrogen-air system is nearly always close to chemical equilibrium. The hydrogen-jet diffusion flame is thus a nonstringent test of the chemical submodel but is an ideal test bed for examining turbulent-mixing models that incorporate the complications of heat release and variable density.

Deviations from equilibrium chemistry were first encountered when experiments began with methane-jet diffusion flames. In these flames, unlike the hydrogen chemical system, the methane chemical system was found to be far from chemical equilibrium. Evidence of local flame extinction was found in the Raman data (major species concentrations and temperature) well before total flame extinction. More recently, flame extinction has been explored by combining the multispecies Raman scattering apparatus with a laser-induced fluorescence system for the OH radical [2]. The simultaneous Raman scattering and laser-induced fluorescence measurements have provided data that have greatly improved our understanding of turbulent flames. When the experimental data are compared with the results of numerical models, it is found that the measured OH superequilibrium is underpredicted. Clearly, one would like to be able to measure other flame radicals such as the oxygen and hydrogen atoms, to provide a more stringent test of turbulent flame models. Also, examination of the data reveals that in many cases the Raman measurements of H\textsubscript{2} and CO are marginal because of low signal level.

The multiple-laser system proposed for the CRF will allow the simultaneous measurement of more flame radicals, and it will increase Raman signal levels. Three of the Nd:YAG lasers can be dedicated to measuring OH, the oxygen atom, and the hydrogen atom by laser-induced fluorescence. The 532-nm output from the remaining seven Nd:YAG lasers can be combined effectively into a single 3.5-J pulse by firing them all within a microsecond to make the multispecies vibrational Raman measurements. This will enhance signal-to-noise in the Raman scattering measurements significantly. Currently, these measurements are performed using a 1-J flashlamp-pumped dye laser. With these improvements in both the laser-induced fluorescence and Raman measurements, the validity of the often-used assumptions of partial equilibrium or steady state can be determined. Accurate
measurements of H$_2$ and CO will be especially interesting for comparison with turbulent-flame models, because they are intermediate species in hydrocarbon combustion.

With the large effective pulse energy from the multiple-laser system, it will be possible to reduce the size of the laser probe volume and still have enough Raman scattered light to yield statistically significant signals. Questions of the effect of spatial resolution on the measurement and previously unresolved probe regions of high shear can then be more fully explored.

3.6.2 Advanced Imaging Techniques for Combustion

The problem of understanding turbulent reacting flows is characterized by both extreme complexity and great practical importance. Part of the difficulty lies in the vast amount of information that must be obtained to completely describe a turbulent flame. Laser diagnostic techniques have proved to be an important tool for probing these complex systems because of their ability to provide nonintrusive in situ measurements. By combining laser scattering with advanced digital cameras, imaging techniques have been developed that provide quantitative data in two and sometimes three dimensions. This information on the spatial distribution of flow structures is critical for understanding interactions of the chemistry with the fluid motion.

Recent studies have demonstrated simultaneous two-dimensional imaging of CH and CH$_4$ in turbulent flames, combining Raman and fluorescence techniques using a single laser operating at one [3] or two [4] wavelengths. These experiments have provided valuable insight into possible approaches to modeling the interaction between turbulence and combustion. The combination of the two-wavelength method with a second laser for simultaneous OH imaging has also been recently implemented [5]. A distributed-reaction-zone model that relates flame zone chemistry to turbulence structure has been shown to be consistent with the data from these latter experiments.

The recent advances in our understanding of turbulent combustion have validated the importance of multidimensional imaging measurements in model flames. It should be noted, however, that our understanding is still in its infancy, and even more complex measurements are needed to maintain progress in the field.
Past advances in laser diagnostic techniques have been closely linked to improvements in laser sources. The availability of multiple, high-power, separately tunable, collinear laser pulses will allow a range of new experiments that will considerably extend the understanding of turbulent flames. Specific examples of the use of the facility for imaging experiments include the following:

- Single large-pulse experiments. Because of the small scattering cross section and low concentration of many of the components of interest, a large laser energy is needed. By combining the output of all the lasers into a single pulse, the lower limit of detectability will be extended for many species, and measurements of additional species will be possible.

- Multiple-species imaging diagnostics. With multiple wavelengths, simultaneous measurements of several species will be possible (e.g., via fluorescence imaging).

- Temporal evolution of turbulent flames. No currently available single laser is able to provide the high-repetition-rate, energetic pulses needed for combustion research. By pulsing the lasers sequentially, a time history of flow development will be obtained.

- Three-dimensional measurements. Turbulent flows are inherently three-dimensional. By forming a series of closely spaced illumination sheets and imaging the scattering from each sheet separately, it will be possible to obtain important information on the topology of the flow structures.

- Combinations of the above. One of the most exciting aspects of the proposed laser system is the flexibility it offers in choosing the wavelength, pulse sequence, and spatial configuration of the energetic laser pulses. Depending on the requirements of the specific experiment, some combination of the above operating modes can be selected.

The availability of the multiple-beam Nd:YAG/dye laser system, together with support personnel to facilitate its use, will foster application of existing techniques, as well as the development of new ones.

3.6.3 Three-Dimensional Imaging of Turbulent Reacting Flows (Femtosecond LIDAR)

The understanding of turbulent reacting flows has been greatly enhanced over the last decade owing to the development of two-dimensional imaging
techniques (see also above). These techniques typically rely on producing a planar-stroboscopic sheet of light with which to illuminate the turbulent system. Either fluorescence or scattering is then collected from the illuminated plane onto a two-dimensional detector system for analysis. The sheet of light projects out a slice through the three-dimensional flow field. One limitation of these techniques is that in many cases information parallel to the sheet but displaced orthogonally is necessary to fully understand the turbulent phenomena. In particular, information on the topology of the structures, such as surface-to-volume ratios, connectedness, and possible fractal dimensions can be studied only by analysis of volumetric data.

To extend the imaging of turbulent flows to three dimensions is a challenge. One solution, as discussed above, has been to use multiple laser beams to illuminate different projections through the flow field and collect the images using a fast electronic framing camera. With this technique, 12 exposures, with 50-ns separation, have been recorded, and a spatial resolution of 0.3 mm has been obtained. In many cases, where one wants to look at large-scale structures and for which about 12 exposures are sufficient, this technique provides suitable resolution, and the multiple-beam Nd:YAG/dye laser system will be ideal for these studies. Higher resolution will be required when looking at a thin flame front that may be less than a millimeter in total thickness, at wall interactions where the flow changes very rapidly near the interface, or at a variety of other structures in reacting flows. A further advantage of the arrangement described here is that it requires only one small window into the combustion environment being studied (since the signal is collected in the backscattered direction) and the number of frames can easily be as high as 100.

The femtosecond laser system offers unique capabilities for high-spatial-resolution imaging. An unfocused 100-fs laser pulse is a sheet of light about 30 μm thick. By recording the two-dimensional backscattering (Mie or Rayleigh)—or, under some circumstances (high light flux resonant with a predissociating molecular state), laser-induced fluorescence—from the pulse as a function of time as it propagates through a turbulent medium, a three-dimensional image will be produced. This is a high-spatial-resolution LIDAR (Laser Infrared Detection And Ranging) arrangement.

The largest signal will come from Mie scattering of particles in a flow. These can be seeded into the flow or can occur naturally (soot). The expected signal levels can be calculated by comparison to the two-dimensional imaging experiments performed at Sandia by Marshall Long of Yale. In his experiments, a 550-mJ laser pulse of 1.4-ms duration was used to illuminate an area of about 0.1 cm² (~300 mm thick and 3 cm tall). During the 10-ns exposure time of the electronic framing
camera, there is an equivalent laser flux of about 4 mJ per pulse per 0.1 cm$^2$. Long reports high signal levels with this level of laser light. In a femtosecond experiment, if a 0.3 x 0.3–cm$^2$ area is illuminated with 1 mJ of laser light, the photon flux will be about the same. Assuming that the backscattering signal is as strong as the sidescattered signal of the other arrangement, one would expect a signal-to-noise ratio similar to that observed in previous experiments; spatial resolution will be better. These considerations should hold for Rayleigh scattering experiments as well.

How is backscattering recorded on such a fast time scale? Electronic framing cameras require about 4–10 ns for an image to be recorded, and this is much too long for envisioned purposes. By using a fiber optic bundle, one can convert a two-dimensional image into a line image and record this information with a streak camera. Ideally, an image would be recorded each 0.1 ps, since that is the duration of the laser pulse (corresponding to every ~30 μm of propagation distance). This is not currently possible, but 0.6 ps is commercially available and 0.35 ps has been reported. Therefore, a resolution of about 100 μm is a reasonable expectation with present technology. Each image will then be stored as a single line of intensity by the streak camera. With present technology, along a single line of the streak camera there is a resolution of about 500, corresponding to a resolution of the image of about 25 x 25, or ~100 μm for a beam diameter of 2.5 mm. In this manner, about 100 frames (~30 line pairs per mm on a 3-mm detector) could be obtained in a single laser shot.

This new technology should allow us to take a new look into the turbulence associated with spark ignition inside an internal combustion engine, as well as to dissect the flame front of a high-pressure turbulent flame. As streak camera technology improves, higher resolution will be possible. The advent of volumetric hologram recording may add new possibilities for the fast recording of images and in the subsequent analysis.

References: Combustion Diagnostics


3.7 THEORY AND COMPUTATION

3.7.1 Theoretical Chemical Dynamics

Highly productive modern scientific research requires broad and vigorous interaction among theorists and experimentalists. In theoretical chemical dynamics, this encompasses a broad range of efforts in developing new methodologies for determining Born-Oppenheimer potential energy surfaces and new dynamical methods for describing molecular processes on these potential surfaces. Methods of surface determination include conventional quantum chemistry, quantum Monte Carlo techniques, reaction path models, and empirical valence bond models; processes on the surfaces can be described by classical trajectory approaches, modified trajectory methods that take into account quantum zero-point energy constraints and tunneling processes, quantum time-dependent propagation methods, reaction as a quantum transition methods, and time-independent quantum scattering methods for inelastic and reactive processes. At the CDF, a major emphasis will be placed on relevance to the understanding of fundamental and combustion-related processes in the choice of system to be studied. Described below are some of the applications of these techniques that are current or planned at LBL, as examples of the benefits that can be reaped in having strong coupling of theorists and experimentalists. At the CDRL, this coupling will be strongly encouraged, and will include both in-house and outside users.

Potential Energy Surfaces. In the study of potential energy surfaces, there are numerous examples of interaction between theoretical and experimental programs. For example, calculations on the electronic structure of the nitrate radical (NO₃) have been stimulated by high-resolution laser-induced fluorescence experiments. Similarly, to provide guidance in interpreting unimolecular decomposition studies of H₂CO, detailed calculations of the potential energy surface in the transition state region, as well as the reaction coordinate, leading to H₂ + CO products and the transition state region leading to H + HCO are needed. Multiconfiguration self-consistent-field (MCSCF) and configuration interaction (CI) approaches are being used in these efforts.
3. RESEARCH OPPORTUNITIES

Likewise recent experimental work aimed at addressing the $\text{O}^{(3P)} + \text{C}_3\text{H}_4$ system and the relative importance of central-carbon versus terminal-carbon attack of oxygen has been aided by MCSCF calculations to delineate the most probable reaction pathways in this system.

Similar opportunities can be foreseen for the future. Theoretical studies connected with many experiments planned for the CDRL require the calculation of electronically excited potential energy surfaces and associated nonadiabatic-coupling matrix elements. Accuracies anticipated from the new experiments will clearly tax the state of the art of ab initio potential energy surface computation and will therefore serve as an impetus for the development of improved methods and algorithms. MCSCF, CI, many-body and Moeller-Plesset perturbation theory, and quantum Monte Carlo techniques will be used to characterize the electronic structure of polyatomic radicals and ions.

The calculation of the properties of complicated aromatics, complicated radicals, and large clusters undergoing excitation, ionization, and dissociation is not at a level of accuracy to be predictive of, or competitive with, experimental measurements. These areas present a range of theoretical problems whose advancement depends on the development of new techniques and methods.

Although there has been significant progress in the calculation of harmonic spectra, the accuracy requirements for transition-state spectroscopy and weakly bound systems consisting of four or more atoms, as well as clusters, dictate the inclusion of anharmonic contributions. Recent advances with collocation and time-correlation quantum Monte Carlo methods are promising developments in this area. Proposed experiments will generate molecules in highly excited rovibrational states that are difficult to calculate accurately, by either quantum mechanical or classical methods.

Clusters present special problems because they readily isomerize and because of their limited stability. Methods for global optimization and for the characterization of multiple minima will be subjects of increased attention. Likewise, the computation of absorption and reaction dynamics for clusters and surfaces is at an early stage and will be subjects of continuing investigation.

**Inelastic Scattering.** To assist interpretation of experiments by Moore on the inelastic processes
time-dependent scattering calculations have been carried out using existing potential energy surfaces and coupling matrix elements for a single collision orientation. The angle chosen (45°) is a compromise between a minimum-energy approach and maximum coupling of the excited state to the ground state. Calculations are planned to improve the potential energy surfaces for known deficiencies, and at other geometries adequate for three-dimensional study of the many inelastic events.

**Reactive Scattering.** Quantum mechanical reactive scattering theory provides a completely rigorous characterization of a chemical reaction. The ability to carry out practical calculations has been stalled for many years, however, because of the nonlocal exchange interactions that occur in reactive scattering. In just the last few years, though, it was discovered by Miller and his coworkers that the S-matrix version of the Kohn variational principle is free of the spurious singularities (also known as Kohn anomalies or false resonances) that plague the more commonly used K-matrix version and that have prevented its practical application. With these spurious singularities eliminated, reactive scattering becomes a very standard quantum mechanical calculation: One chooses basic functions, computes matrix elements of the Hamiltonian, and then performs a standard linear algebra calculation (matrix inversion).

Using this methodology, Miller's group has computed the first integral and differential cross section for the \( \text{H} + \text{H}_2 \) (para) \( \rightarrow \) \( \text{H}_2 \) (ortho) + \( \text{H} \) and \( \text{D} + \text{H}_2 \rightarrow \text{HD} + \text{H} \) reactions, the latter one being motivated by a comprehensive new set of crossed molecular beam experiments being carried out by Lee and his collaborators. This is permitting a comparison of theory and experiment for this fundamental reaction at an unprecedented level of detail—i.e., state-to-state differential scattering cross sections. It shows the degree to which modern chemical physics can measure, and calculate from first principles, the most fundamental characteristics of a chemical reaction.

A general and straightforward methodology is thus now available for carrying out rigorous quantum scattering calculations for chemical reactions. It should be possible to carry out such calculations for a number of three-atom reactions (i.e.,
A + BC → AB + C), and some four-atom reactors (e.g., H + H₂O → H₂ + OH) will probably be accessible soon.

The situation is reminiscent of the early days of "quantum chemistry": the basic methodology has become clear, and many practical developments to enhance its efficiency can now be expected. With these developments, and with increasing computer power, the class of chemical systems that can be treated rigorously will continually grow.

**Photodissociation.** The calculations for photodissociation require the solution of a scattering problem and a simple overlap between the scattering wave function and a bound-state wave function. The new abilities that have recently been developed for carrying out inelastic and reactive scattering thus make it possible to deal with a variety of these problems. A specific application has been the photodetachment of the H₂F⁻ complex:

\[
\text{H}_2\text{F}^- + \text{hv} \rightarrow \text{H}_2 + \text{F}, \text{HF} + \text{H} + \text{e}^-
\]

These calculations were carried out as a result of experiments by Neumark and his coworkers, in which the energy distribution of the electrons reveals resonance structure in the neutral scattering system, H₂ + F → HF + H.

Calculations of continuum resonance Raman cross sections, e.g.,

\[
\text{ABC}(v) + \text{hv} \rightarrow [\text{A} + \text{BC}] \rightarrow \text{ABC}(v') + \text{hv}'
\]

can also be carried out with these methods.

For polyatomic systems with energy level spacing too close for predictions of product vibrational distributions by means of available full quantum methods, one can use an adiabatic theory that treats photodissociation as a quantum transition between quasidiabatic (diabatic) states. The method includes important contributions from final-state interactions. Obtaining product distributions requires the evaluation of Franck-Condon-type matrix elements.

**Theoretical Dynamics of Polyatomic Systems.** There will always be chemical systems of interest that are too large for completely vigorous quantum mechanical treatments. (At present this applies to systems involving more than three or four atoms.) A variety of classical and semiclassical methods have been developed for describing reactions of such systems, and research continues. Recently, for example, Miller and his coworkers developed a model for constraining chemical trajectory simulations so as not to violate quantum zero-point energy conditions in any
modes of the molecule. A model was also developed for incorporating tunneling effects directly into a classical trajectory simulation. The reaction path Hamiltonian is also a general approach for describing reaction dynamics in polyatomic systems. It has been adopted by many research groups and is particularly well-suited for use with ab initio electronic structure calculations.

Statistical theories are also often useful for treating dynamics in complex systems. Recently, for example, Miller developed a random matrix-theory-based transition-state model for describing the distribution of state-specific unimolecular rate constants for formaldehyde decomposition. This theoretical model provides an excellent description of Moore’s extraordinary set of experiments, which have determined unimolecular reaction rates for hundreds of molecular eigenstates of highly vibrationally excited formaldehyde.

It is clear that future dynamical applications will make full use of this array of classical, semiclassical, and statistical methodologies.

3.7.2 Combustion Modeling

In the coming decades, as the U.S. strives to achieve energy efficiency while minimizing environmental damage from combustion devices, computational combustion modeling will play an ever-increasing role. Indeed, it is detailed models that allow the technology transfer from fundamental chemical dynamics experiment and theory into the combustion community. This link between the molecular and the macroscopic will be the driving force behind research at the CCCS.

The current generation of computers is slowly allowing the coupling of molecular-level chemistry with the macroscopic fluid and thermal calculations required to accurately model realistic combustion devices, as has been demonstrated by Sandia’s flame-modeling research. Many of the limitations on modeling realistic combustion systems, such as computer speed and memory, are readily addressed by moving to new computer architectures, specifically, to massively parallel machines that not only can be significantly faster than today’s vector supercomputers, but also have significantly more distributed memory—thus allowing the solution of two- and three-dimensional problems, as well as more accurately addressing fundamental questions in turbulence and coupled kinetics. This represents an area of research at the CCCS that will have an immediate impact on the combustion community. In addition, molecular-level information needed in these models is oftentimes not available experimentally, and must be either extrapolated from
3. RESEARCH OPPORTUNITIES

similar species or calculated from first principles using theoretical chemistry. Bringing these methods to the point where they can routinely give input to the models will be another focus at the CCCS, and will involve fundamental research, as well as the migration of theoretical methods onto next-generation massively parallel computers that will have the computational power necessary to make chemically accurate predictions.

Macroscopic numerical models can be divided into two distinct regimes. In the first, the fluid mechanics are straightforward enough to be essentially exactly soluble, and can therefore be coupled with complex chemical kinetic mechanisms. In the second, the fluid motions are essentially turbulent and are therefore inherently more difficult to treat. In the former case are flame models, well-mixed reactor models, and ignition models. The current state of the art typically solves one spatial dimension, which, by use of symmetry in the experiments, can be mapped onto realistic geometries. These models are related directly to diagnostics experiments in combustion systems, and insights into the complex interrelationships among fluid, thermal, and chemical processes governing the process are thus obtained. Fundamental experimental and theoretical investigations have had, and will continue to have, tremendous impact on the kinetics included in these models, where detailed mechanisms, rate constants, and thermodynamic properties are required for each species present. Even for simple hydrocarbon flames, hundreds of species must be considered. Because experimental data on these often are incomplete, theoretical chemistry is playing an increasingly important role.

The next generation of flame models will branch off in several different directions. First, the calculations soon will be routine enough to be treated on next-generation computers, making real-time diagnostics on embedded processors accessible to industry. Thus, feedback loops can be utilized, increasing fuel efficiency as well as reducing pollution. In addition, the models will be extended to two and three spatial dimensions, making many difficult industrial processes treatable with these combustion models. To obtain both the processing power required and the storage necessary for large multidimensional grids, these new models will need to be adapted to the next-generation massively parallel computers. Present-day massively parallel computers are already as powerful as current supercomputer technology (e.g., the Cray Y/MP-864), in terms of both total computer power and total available memory. In addition, because these new machines are usually more cost effective, this migration process will significantly increase the utility of the models for the combustion community.
The second category of combustion models is for turbulent systems. Currently, these models can generally provide results useful for engineering purposes. One of the most crucial shortcomings is the inability to accurately predict departures from chemical equilibrium in highly turbulent flows. A method we are exploring for furthering basic understanding of this problem is the probability density function (PDF) approach, which allows exact treatment of the chemical kinetics term.

For problems involving multiple species, solution of the PDF equations is feasible only by Monte Carlo simulations, in which the PDF is represented by a collection of statistical events. As with all Monte Carlo approaches, many events must be computed for averaging. The effects of turbulent mixing, chemical reactions, and molecular mixing on the PDF are simulated by stochastic processes. It is the simulation of the chemical reactions that consumes the bulk of the computer time. Using present computational equipment and methodologies, it takes more than 1000 hours on a Cray X/MP to simulate a turbulent jet flame with only four chemical species.

One avenue that will allow the solution of these Monte Carlo simulations with many reacting species is to adapt the codes to massively parallel computers. Monte Carlo simulations are ideally suited to this type of architecture, since each processor can run one grid point, and all points can be run in parallel. Thus, not only do we gain an $n$-fold speedup for $n$ grid points, but we also can efficiently utilize the tremendous amounts of distributed memory in these machines to include additional chemical species. Each processor only needs access to the data that is relevant to the local grid point, and to those interacting with it. Thus, we expect, for the first time, to move turbulent-reacting-flow modeling to the level of today's laminar flow models—that is, treating the full set of chemical kinetics.

In the long term, rigorous theoretical studies using the instantaneous Navier-Stokes equations, coupled with detailed chemical kinetics, are desirable. However, because of the large spatial and time scales involved in turbulent reacting flows, these methods exceed present-day vector supercomputer capabilities by orders of magnitude. Currently, projects are under way in the U.S. to build massively parallel computers with teraflop ($10^{12}$ computations per second) computing power. Access to this class of computer, together with the required numerical methods, would allow rigorous simulations of turbulent reacting flows.

All of these modeling efforts require detailed knowledge of thermochemical properties of each species and reaction mechanisms, as well as reaction rates
3. RESEARCH OPPORTUNITIES

between all species. While experimental measurements are crucial to obtaining accurate information, it is often lacking and can more readily be obtained utilizing theoretical methods. At Sandia, BAC-MP4 methods are currently being used to obtain thermochemical information needed in the models, with a typical accuracy of several kcal/mole. To obtain reaction pathways and mechanisms, a combination of SCF, CAS, MP2, MP4, and CI methods are used, and at times, it is difficult to balance the goals of chemical accuracy required by the dynamics to subsequently obtain rates, with the cost of the method and the total elapsed time needed to obtain results. Once the pathways are determined, reaction path Hamiltonian methods, variational transition state theory, RRKM theory, and classical and quantum dynamics are employed to evaluate the rates of reaction or of energy transfer processes (often required to interpret the diagnostics experiments).

Next-generation massively parallel computers will have a tremendous impact on both the accuracy of these calculations and their impact. Currently, we are limited in the number of pathways and species that can be investigated, because the determination of a reaction pathway requires the evaluation of not only a hundred or so energies, but also second derivatives, and the elapsed time to obtain this information can be months. Having accurate quantum chemical methods available on computers that are an order of magnitude faster would allow examination of tens of reactions per year, instead of just a few. In addition, massively parallel computers will increase the total computing power available, in terms of both CPU cycles and memory, thus enabling the use of increasingly accurate theoretical methods and increasingly large basis sets, leading in turn to more accurate potential energy surfaces and dynamics. In addition, it will be possible to employ increasingly accurate dynamics calculations, bringing quantum dynamics to systems of interest to the combustion community. Thus, we will also test our understanding of the fundamental physical processes, by comparing the results of these calculations with accurate chemical dynamics experiments.
4. OPERATIONS PLAN

The Combustion Dynamics Facility is a multisite initiative that will benefit from the unique scientific, technical, and managerial resources available at LBL and SNL. To be effective, the management plan of the CDF must comprise three important elements. First, responsible, accountable line management must be empowered at each site to ensure that operations are conducted in a manner consonant with the facilities’ goals. Each institution will therefore assume management responsibility for research and facility operations at its site. As shown in Fig. 4-1, the CDRL at LBL will be managed within the Materials and Chemical Sciences Division; whereas, at SNL the CRF and the CCCS will be managed within Sandia’s Combustion and Applied Research Directorate. At each site, a single director will be appointed.

![Diagram of CDF organization chart]

Figure 4-1. A schematic organization chart for the CDF, showing the lines of authority at both LBL (for the CDRL) and SNL (for the CRF and the CCCS), and indicating the integrative roles of the three advisory committees.
Second, the management plan must provide an active means for integrating activities at the two institutions. Toward this aim, a Liaison Committee will be put in place to integrate the scientific and user programs of the two institutions. This committee, staffed by scientists and managers from LBL and SNL, will promote a close relationship between the facilities at the two sites, using a variety of approaches, including joint scientific meetings, workshops, reciprocal visits, joint research programs, and sharing of students and postdoctoral fellows. The Visitors Program Coordinator (see Section 4.3) will be a member of this committee. Liaison activities are currently being carried out by Robert Johnson and Andrew Kung of LBL and Stephen Binkley and George Fisk of SNL.

Third, review and advisory structures must be put into place to assist line management at each institution in charting the long-term course of the CDF, as well as to guide the selection of research conducted, so as to maximize the scientific impact of the joint facility. To advise management on policy matters and long-term issues affecting the CDF, a Steering Committee will be created. As shown in Fig. 4-1, this committee will be appointed by and will report jointly to the Director of LBL and the President of SNL. The Steering Committee will be composed of nine members drawn from distinguished scientists and engineers, predominantly from the fields of combustion research, physical chemistry, laser chemistry, spectroscopy, and advanced laser physics and from the scientific management ranks of industry, universities, and national laboratories. The Committee will provide advice on all aspects of the CDF, including its research program, its facilities and their utilization, and its policies regarding facility users and other visitors. The Committee will also prepare an annual, written critical evaluation on these matters. The Steering Committee will be put in place well before actual project construction begins to provide external policy guidance. The charter for the Committee is reproduced in Appendix A.

When funding becomes available for the detailed design of the CDRL experimental facilities, a Program Review Panel will also be put in place to make specific recommendations regarding the disposition of all proposals for the development and use of facilities. This panel will advise the LBL Director and the SNL President, through the Director of the CDRL and the Director of the CRF and CCCS, respectively. Complete details of the proposed working of this committee are provided in Appendix B.
4.1 CDRL MANAGEMENT AND OPERATIONS

The directors of the CDRL (at LBL) and the CRF and CCCS (at SNL) will have line responsibility and authority within their respective institutions, as shown in Fig. 4-1. SNL has operated the CRF successfully for the chemistry and combustion community since 1980; as described in Section 4.2, there will be little change in its management and operation plan. The managerial approach for the CDRL was developed from LBL experience in operating national facilities for a broad range of scientific users and from extensive discussion with SNL managers. The resulting plan is described below.

4.1.1 Management Structure

The CDRL management structure was designed to promote excellence in well-focused, multi-investigator chemical physics research, to build a strong visitor program, and to advance the application of new instrumentation for molecular studies. Management and staff include the following:

- The Director of the CDRL
- A Deputy Director of Operations, responsible for matters related to user support and equipment operation
- A Safety Committee to review experiment design safety, operator safety criteria, and operational safety practices
- Scientific and technical staff, including principal investigators, staff scientists, operations staff, user support staff, postdoctoral associates and graduate students, and technical staff

The CDRL Director will have overall responsibility for the core research program and the management of the facility, as well as its relationships to the facilities at SNL, the ALS Chemical Physics Participating Research Team, and other institutions. Lines of responsibility extend directly from core program areas to the CDRL Director. In coordination with the Director of the CRF and CCCS, and with the help of the Liaison Committee, the CDRL Director will implement policies to effect productive research and full facility utilization. He will have complete responsibility for staffing and budgeting of the facility.
The CDRL Director is appointed by the Director of the Materials and Chemical Sciences Division, who reports to the LBL Director. Yuan T. Lee, a faculty senior scientist at LBL who has a distinguished record of scientific accomplishments in chemical physics and a proven record of scientific leadership, has assumed the position of CDRL Director.

The CDRL Director will appoint a Deputy for Operations, to whom he will delegate authority to oversee day-to-day facilities and instrument operations, to ensure effective support of users and continuity of services. The Operations Deputy will be responsible for the safe operation of equipment, for user coordination, and for training and qualification of users and support staff. The operations staff will be responsible for IRFEL operations, beamline operations, laser operations, and the development and maintenance of molecular beam machines and other experimental station instrumentation.

4.1.2 Operations

The CDRL will be operated as a user facility with staff to provide operations support and to assist in the development of instrumentation. The IRFEL will be a dedicated national user facility with experimental stations available to outside users, core researchers, and collaborative research teams. It is planned that qualified technical staff be available for around-the-clock operation. During all operating hours, the IRFEL control room will be operated by technically qualified personnel. In the adjacent ALS, operators will also be present, including engineering support staff. All operations, including shift changes, will be subject to periodic review and will be conducted within controlled Operational Safety Procedures.

Operational support for scientific programs will include the dedicated staff of scientists, postdoctoral associates, and an active graduate student program. The CDRL Director and the Operations Deputy will encourage a close working relationship among collaborators, visitors, and students. Daily operations are expected to be characterized by an active interplay of multidisciplinary research teams, with essential theoretical, experimental, and instrumentation development staff closely involved.
4.1.3 CDRL Users' Organization

A users' organization will provide an additional framework for interaction between users of the CDRL and its management and will act as a participating research team (PRT) at the ALS. In representing the interests of researchers to CDRL management, this organization will make known the needs and desires of the users regarding operating policy, user support, and other issues. It will also provide a mechanism for CDRL management to inform users of current and future plans and for cooperation in shaping such plans. Acting as an ALS PRT, the users' organization will interact with ALS management, in conjunction with CDRL management. The draft charter for the CDRL users' organization is provided as Appendix C.

4.2 CRF AND CCCS MANAGEMENT AND OPERATIONS

4.2.1 Management Structure

Programmatic management of the Basic Energy Sciences–supported activities within the enhanced CRF and CCCS will be provided in a fashion consistent with the management structure currently in place at the CRF. Briefly, J. S. Binkley will serve as the project manager for the combined CRF and CCCS activities. He will be charged formally with ensuring that the programs meet their technical and visitor-related objectives, and with serving as the primary point of contact with the DOE's Office of Basic Energy Sciences. Additionally, the project manager will be responsible for promoting a productive relationship between SNL and the CDRL at LBL.

Where appropriate, leaders of subprojects will be appointed (e.g., for facility operations, computing support, etc.). These persons will be accountable to the project manager for accomplishing the objectives of their respective parts of the overall project.

To provide prompt dissemination of scientific and technological results to the broadest possible outside community, the project manager will be assisted by the supervisor of technology transfer, T. Michael Dyer.
4. OPERATIONS PLAN

4.2.2 Operations and Resource Management

Continuing operation of the CRF and CCCS, in terms of managing both personnel and facility resources, will be the responsibility of W. J. McLean, manager of the Combustion Science and Technology Department. He will ensure that the facility lasers are adequately staffed and available as needed to qualified users; that users have adequate technical, computational, and secretarial support; and that user-staff interfaces are effective. He will continue and extend the management practices already in existence, which have led to strong in-house research and a vigorous visitor program.

4.3 VISITORS PROGRAM

The visitors program is the heart of the Combustion Dynamics Facility. Its major objective is to provide a full-service, responsive, and flexible environment for visitors to the CDF facilities at LBL and SNL. Visitors will have access to all CDF capabilities, either independently or in collaboration with in-house CDF research staff. Within the CRF, the existing collaborative research mode will be continued and enhanced. Within the CDRL, the CRF collaborative mode will be adapted to provide maximum opportunity for visitors to interact with one another and with the CDRL research staff. Following the advice of a review committee chaired by Stephen R. Leone, the modes of user involvement at the CDRL have been clarified to provide sharper delineation among external user experiments, in-house research, and collaborative projects, as described below. Resources will be made available for each mode, both for design and specification of the experimental stations and for ongoing support of research.

Further, because the CDF will be a national user facility, all of the experimental stations in the main hall will be available to all qualified investigators on the basis of priorities established by the Program Review Panel (PRP) following open competition. The best utilization of the facility will result if experimental stations are not duplicated unnecessarily, which might happen if users (either in-house or external) could use only stations they had designed and built. The PRP will follow the ratio 2:1:2 in allocating research time among independent external users, in-house researchers, and collaborative researchers (see below).

An essential element of the visitors program is an individual to be responsible for building up the base of external users and further defining the visitors program itself. The Visitors Program Coordinator will normally be a
member of the CDF Liaison Committee; the details of the job duties for this position are provided in Appendix D. This position will be filled on a permanent basis once the project becomes part of DOE planning. Andrew Kung, who formerly headed the San Francisco Laser Center, will serve in an acting capacity until then.

4.3.1 Research Modes

Independent External User Experiments. Visiting scientists may propose new research that makes use of the CDF's resources, independently of in-house investigators, and for which the visitors retain full intellectual ownership. Resources for visitors to design and develop two experimental stations have been requested as part of the construction project. Awards will be made by the Director of LBL, following competitive review by the PRP.

In-House Research. A strong in-house research program is essential to the success of the CDF. The CDRL proposal therefore includes individual laboratories, separate from the main experimental hall, for approximately six in-house principal investigators. In addition, offices and computer access will be provided for in-house theorists. Both experimental and theoretical in-house projects and programs in this part of the CDRL will host visiting principal investigators and students in a fashion similar to that typical for traditional academic visitors. For in-house research, it is expected that the major ideas will be those of the resident scientists and that visitor research will be derivative.

In-house experimentalists will relocate and modernize an existing molecular beam chamber in the main hall of the CDRL.

Collaborative Projects. Visiting scientists and CDF investigators may jointly propose new research, intellectual ownership of which will be vested in both in-house and visiting scientists. Development of the requisite equipment will occur with members of the collaborative research group resident at the CDF. The construction budget request for the CDF identifies resources for two experimental stations to be developed in this collaborative mode. These resources will be allocated to proposing teams by the Director of LBL, following competitive review by the PRP.
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4.3.2 User Support

It is estimated that when fully developed the CDRL will involve approximately 50 full-time visitors. It is important to note that operating funds for the CDRL are envisioned as new resources for the DOE's Division of Chemical Sciences (DCS); they should not result from the redistribution of funds from current programs. A substantial fraction of the total research funding needed—30% of the estimated external user program—will be administered through the CDF; the rest will be solicited via specific research proposals to the DOE and other agencies.

Direct support administered through the CDF related to the use of experimental stations will include the following:

- Funds for postdoctoral fellows and graduate students, to enable quick responses to requests for short-term visits in which, for example, "proof-of-principle" experiments will be conducted to support proposals for longer-term research activities

- Supplies and noncapital equipment for experiments (calculated as a percentage of salary support based on LBL and SNL experience)

- Supplemental costs of travel and living expenses, especially for those, such as visiting graduate students, who may have only marginal independent support, subject to review by the PRP

- Costs associated with the CDF Fellows Program (see below)

- Salaries of scientific support staff, technicians, and other CDF managerial and administrative staff

Professional staff and technicians will work closely with visiting user groups to develop and execute experiments at the CDRL. Although their primary function will be to provide support, they will be encouraged to participate actively in research conducted by the user groups. Current plans for the professional staff include two ALS beamline–molecular beam apparatus experts, one FEL optical expert, one conventional laser expert, and one computer software–interface expert; this is viewed as the minimum number of staff specialists required to successfully operate the CDRL. In collaborative projects involving in-house groups and an outside group, some technical expertise and support will be provided by the students and postdoctoral fellows of the associated in-house group.
As the research requirements of in-house and external users evolve, there will be a need to update experimental-station capabilities. Further, it is anticipated that stations will require minor modifications from time to time to meet the needs of particular experiments. The CDF proposal includes annual operating and capital funds to cover these needs. Recommendations for these expenditures will be made by the PRP; allocations will be made by the LBL Director. Users of the CDF also may obtain funds to modify or redevelop experimental stations by direct application to the DOE or other agencies.

In keeping with widespread practice at national user facilities, salary support will not be administered through the CDF for visiting researchers, except as described above and for the Fellows Program described below. Appendix E describes the process leading to approval, funding, and execution of a typical CDF research project involving visitors.

4.3.3 CDF Fellows Program

A visiting fellows program will be created to provide partial salary support and supplies and expenses for scientists from other institutions to work at the CDF. Participants in this program will typically have some matching support from home institutions, consistent with sabbatical-like appointments. Based on experiences with similar programs at other institutions, we anticipate that this program will permit four to eight fellows to participate in CDF research, if funded at the requested level. Fellows will be solicited through announcements in the national and international scientific media; fellowships will be awarded by the LBL director, based on recommendations made by the CDRL Director, who will review applications in conjunction with the PRP. This program is described in detail in Appendix F.

4.3.4 Visitor Accommodations

The Lawrence Berkeley Laboratory does not have on-site housing and is prevented by its contract from building housing on site. Nevertheless, the Laboratory is committed to making it as easy as practical for visitors to work at the CDRL; assistance is available to users seeking to secure either short- or long-term housing. The results of market surveys and issues related to convenient dedicated housing are discussed in detail in Appendix G. At SNL, existing methods to provide visitor accommodations, developed at the CRF, will be continued.
4. OPERATIONS PLAN

4.4 EDUCATION PROGRAMS AND OUTREACH

The educational goals of the CDF include improving the quality of chemical physics education for graduate and undergraduate students and expanding opportunities for women and minorities. The CDF will offer new opportunities for undergraduates and graduate students through experimental and theoretical research programs, seminars, and workshops. LBL faculty scientists are mentors to graduate students, at the same time encouraging them as essential partners in research. Completion of the Ph.D. requires five to six years, during which time the student publishes several papers and initiates a dialogue with other members of the scientific community. During the final years of training, graduate students advance new ideas and technical solutions and have accrued extensive experience with research equipment. The research programs at the CDF will make extensive use of qualified graduate students from all participating institutions, and they will be active members of research teams and collaborations.

Outreach activities for women and minorities will have the objective of improving the opportunities and capabilities of these groups. Specific attention will be given to Black and Hispanic groups, which are significantly under-represented in chemistry. CDF management and staff will work in close conjunction with LBL’s Center for Science and Engineering Education and with groups on the Berkeley campus, including the Black Engineering and Science Association, the Hispanic Engineers and Scientists Association, and the Minorities/Women’s Office of the Graduate Assembly. CDF staff are also closely involved with the Lawrence Hall of Science, an innovative science education and curriculum development center. This involvement will help to communicate the excitement of studying chemical dynamics at its most fundamental level, thus broadening appreciation of physical chemistry at early stages of chemistry education.

4.5 KNOWLEDGE AND TECHNOLOGY TRANSFER

Because the CDF is focused on basic and applied combustion research, it will contribute to a better U.S. position in international economic competition in chemical, fuels, fuel use, and control technology industries. This contribution will take the form of short-term transfer to industry of research findings, instrumentation technology development, and a trained staff, as well as such long-term enhancements as a strengthened scientific base in combustion dynamics and the improvement of cross-disciplinary interactions. An important technology
transfer mechanism is the training of graduate students who later are hired by industry.

The CDF will be open to qualified scientists from industry, universities, and other government laboratories. In addition, scientific workshops will be organized on aspects of physical chemistry and reaction dynamics and on advanced photon instrumentation for chemistry, including IRFELs and chemical sciences beamlines. The workshops will provide focused opportunities for leading national experts and advanced students to engage in discussions and to exchange information. Distribution of workshop proceedings and reports will further disseminate information. Occasionally, the workshops will have the tutorial character of the short courses previously given by the staff of Sandia's combustion program. Experience has taught that the short-course format is an excellent one for communicating to interested users the expertise required to implement new optical diagnostic techniques, for instance.

The transfer of technology from the CDF to industrial and other users will follow patterns similar to those that have developed in the combustion program at SNL. Important paths for technology flow originate both in the development of new techniques and equipment and in the generation of new fundamental scientific information. Application of modern optical diagnostic techniques to problems in combustion often requires developing novel hardware. Within the past few years, Sandia has developed and transferred to industry two important technologies: single-mode, diode-pumped Nd:YAG lasers that are used to stabilize the frequency of pulsed Nd:YAG oscillators through the technique of injection seeding, and single-pass, permanent-magnet Faraday isolators that prevent damaging feedback into laser components and do not require external power supplies. Both of these devices were commercialized by small companies and are now successful products.

The information generated in research programs often has direct bearing on applied problems. Participation in fundamental studies of nitrogen combustion chemistry led Robert Perry to conceive the RAPRENO_x process for removing NO_x from exhausts. The DOE allowed Perry to assume the patent for the process, and he how heads Technor, a company established to commercialize it.

The initial technological goals of the CDRL will be to develop an IRFEL, advanced chemical physics beamlines, and advanced lasers, detectors, and molecular beam apparatus for the scientific program. Although central to CDF research, these technologies and their associated R&D programs will be important to other fields as well. For instance, development of advanced VUV lasers and new IRFEL components and configurations will be useful to the research and testing
instrumentation market. Likewise, some of the analytical goals of the CRF are similar to those of the chemical process industry, including the precise determination of molecular species in reaction processes. Spin-off developments will include, for example, the development of ultrafast detectors, fast pulse-switching systems, and highly sensitive IR photomultipliers.
5. FACILITIES

In this section, we briefly describe the special facilities that are planned for the CDF and highlight their special characteristics. All of the facilities will be made available to users in the manner described in the previous section. A detailed design effort is under way for the CDRL, and a Conceptual Design Report has been submitted to the Department of Energy, as required for funding consideration as a construction project. All of the facilities can be operated independently, but many will also be operated synchronously in experiments that require the simultaneous utilization of two or more special facilities. In order to accomplish this, for example, the RF used to drive the IRFEL and the picosecond tunable lasers will be derived from the master RF oscillator that drives the ALS storage ring. Since this master oscillator will be used to synchronize all three photon sources, they could be synchronized to within a few picoseconds of one another.

The proposed facilities include

At the LBL site:

- An IRFEL optimized in the 3- to 50-\(\mu\)m wavelength region for chemical sciences research
- An ALS undulator beamline and a bending magnet beamline, both targeted for 6- to 30-eV operation
- Two advanced laser systems and several commercial lasers and accessories
- Several experimental stations, fully equipped with molecular beam apparatus, detection equipment, and data acquisition systems
- Computer hardware, as well as high-speed links to the SNL supercomputers for theoretical computation
- A laboratory facility to support and provide utilities, safety systems, and necessary space for a broad community of users to conduct studies
5. FACILITIES

At the SNL site:

• A femtosecond laser system for studying ultrafast processes and new approaches to three-dimensional imaging

• A versatile multiple-beam Nd:YAG/dye laser system with the necessary hardware for operating in a bunched mode or a fast-framing mode

• Laboratory and office space to house the new laser systems and to accommodate new visitors, as well as to improve staff-user interaction

• A CCCS building to provide office and computer space for both in-house and visiting researchers to conduct advanced computational studies

The following sections provide a provisional description of the technical facilities, especially those features of interest to potential users of the CDF. However, the configuration and characteristics of the facilities actually implemented, while comparable to those described below, may differ in detail, as designs are refined and as user requirements become better defined.

The conventional facilities are briefly described in Appendix H.

5.1 FACILITIES AT THE CDRL

5.1.1 Infrared Free Electron Laser Facility

The IRFEL has been designed to provide quality photons for spectroscopic and dynamics studies. It consists of an RF linear accelerator, an undulator, and an optical cavity. By using three different electron beam energies, one can tune the IRFEL to cover the wavelength range from 3 μm to longer than 50 μm. Broad, continuous tuning is accomplished by fully automated adjustment of the gap of the undulator magnet for each electron energy. The micropulse energy is 100 μJ for 50-MeV operation; the pulse duration will be 10–50 ps. A macropulse of about 100-μs duration consists of about 3600 micropulses. The macropulse repetition rate is 50 Hz. This gives a maximum average power of 18 W. A preliminary summary of the characteristics is given in Table 5-1. Table 5-2 provides more details regarding the expected performance for one setting of the electron pulse duration (10 ps) and pulse charge (1 nC). Figure 5-1 is a schematic, showing the layout of the basic components of the IRFEL.
Table 5-1. Preliminary summary of IRFEL characteristics.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength coverage</td>
<td>$3 \mu m \leq \lambda \leq 50 \mu m$</td>
</tr>
<tr>
<td>Micropulse energy</td>
<td>$100 \mu J$ at $50$ MeV ($3$–$8 \mu m$)</td>
</tr>
<tr>
<td>Micropulse duration</td>
<td>$\sim 10$ ps</td>
</tr>
<tr>
<td>Micropulse rep rate</td>
<td>$36.6$ MHz</td>
</tr>
<tr>
<td>Macropulse duration</td>
<td>$100$ $\mu s$</td>
</tr>
<tr>
<td>Macropulse rep rate</td>
<td>$50$ Hz</td>
</tr>
<tr>
<td>Average power</td>
<td>$18$ W</td>
</tr>
<tr>
<td>Bandwidth</td>
<td>Near transform limited ($\Delta \lambda/\lambda = 0.001$ for $\lambda = 3 \mu m$ and $10$-ps pulse duration)</td>
</tr>
<tr>
<td>Bandwidth Stability</td>
<td>$\leq 0.001 \lambda$</td>
</tr>
<tr>
<td>Intensity Stability</td>
<td>$\leq 0.1$</td>
</tr>
</tbody>
</table>

Table 5-2. IRFEL performance for a 10-ps, 1-nC electron pulse, based on the configuration of Fig. 5-1. The calculations assume a total optical cavity loss of 10% and outcoupling of 5%.

<table>
<thead>
<tr>
<th>Wavelength ($\mu m$)</th>
<th>Electron energy (MeV)</th>
<th>Cavity detuning ($\mu m$)</th>
<th>Bandwidth (%)</th>
<th>Micropulse energy ($\mu J$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>51.3</td>
<td>14.1</td>
<td>0.09</td>
<td>83</td>
</tr>
<tr>
<td>5</td>
<td>51.3</td>
<td>23.7</td>
<td>0.15</td>
<td>96</td>
</tr>
<tr>
<td>10</td>
<td>51.5</td>
<td>88.7</td>
<td>0.14</td>
<td>91</td>
</tr>
<tr>
<td>8</td>
<td>31.4</td>
<td>41.4</td>
<td>0.26</td>
<td>59</td>
</tr>
<tr>
<td>13.3</td>
<td>31.4</td>
<td>92.5</td>
<td>0.25</td>
<td>57</td>
</tr>
<tr>
<td>26.7</td>
<td>31.4</td>
<td>207.6</td>
<td>0.13</td>
<td>62</td>
</tr>
<tr>
<td>25</td>
<td>17.8</td>
<td>170.4</td>
<td>0.14</td>
<td>35</td>
</tr>
<tr>
<td>35</td>
<td>17.8</td>
<td>339.0</td>
<td>0.12</td>
<td>34</td>
</tr>
<tr>
<td>51.7</td>
<td>17.8</td>
<td>722.8</td>
<td>0.16</td>
<td>28</td>
</tr>
</tbody>
</table>
Figure 5-1. Basic components of a linear accelerator–driven FEL (not to scale).

Figure 5-2 describes the temporal characteristics of the IRFEL output. Each micropulse can be synchronized with a VUV pulse from the ALS beamlines and/or with the actively mode-locked picosecond lasers in the experimental hall. Picosecond-scale time delays between these pulses can be achieved by adjusting the relative phase of the RF signal being fed into each device or by spatial delays. The macropulse repetition rate will be matched to the repetition rate of the conventional nanosecond laser in the experimental hall (not be exceed 60 Hz because of electrical power limitations).

Among the design goals of the IRFEL are wavelength and timing stability and minimal jitter for the output, since these characteristics are essential for scientific applications. The following steps are being taken to ensure the best possible performance at reasonable cost. First, we have determined a set of tolerance specifications for the required electron beam stability. Thus, for example, the slow jitter in the electron beam energy needs to be limited to $5 \times 10^{-4}$. Second, these requirements are met by carefully choosing the accelerator subsystems (gun, buncher, klystron, accelerating structure, etc.), and by employing a sequence of feedforward and feedback techniques. The electron beam transport from the linac to the undulator is designed to be fully achromatic and nearly isochronous to preserve the beam quality and stability. Third, the length of the optical cavity will be controlled
- Optical pulse: mimics the electron pulse, e.g., electrons pulse at 36.6 MHz, 100 μsec long at 50 Hz rep rate

Figure 5-2. A schematic illustration of the temporal characteristics of the IRFEL output.
accurately, to a dimension slightly shorter than the value that matches the
micropulse repetition rate, for optimum spectral purity and stability.

The IRFEL will be located in the basement of the CDRL building, along with
its RF driver and power supplies. The control electronics and terminals will be in a
temperature- and humidity-controlled room adjacent to the CDRL experimental
hall. The electron beam parameters will be set and monitored by specially trained
operators, three shifts per day. Changes to the electron beam settings will be done
upon request from the user. Adjustments of the optical cavity alignment, as well as
wavelength tuning, will be controlled by the user at the experimental station, via
software commands. An optical transport system consisting of metal mirrors and
image-relaying lenses will be used to direct the output beam from the basement to
the experimental hall and to other laboratories within the building.

5.1.2 ALS Undulator Beamline and Bending Magnet Beamline

Several example beamline designs have been developed to demonstrate the
level of performance that can be expected. Here we describe an undulator beamline
based on a U10.0 undulator and another beamline based on a bending magnet
source. These two beamlines are operated independently and can thus be used
simultaneously. The capabilities they offer are somewhat complementary: The
bending magnet offers wider spectral coverage, fast and easy tuning, and greater
polarization control than the undulator, at the cost of about a factor of 30 in flux and
beam divergence for comparable operating conditions.

The wavelength coverage, resolution, flux, and polarization requirements of
the various user groups were studied when designing the U10.0 undulator and its
beamline. The principal user requirements are fourfold:

• Photon energy range of 6–25 eV in the first harmonic. The low-energy end of this
range overlaps the capabilities of intense laser sources; the high end allows
exploration of valence-shell processes in molecules.

• Intensity of a least $10^{12}$ photons per second at 0.1% bandwidth. This is required for
a wide variety of measurements that involve sampling of dilute molecular-beam
targets for studies of radicals, clusters, and complexes.
• High brightness combined with a tightly focused beam. "Two-color" experiments involving the ALS beam and a laser beam, for example, will involve an interaction volume whose linear dimensions are of the order of 50 \mu m.

• Resolving power of at least 50,000. This requirement must be met to allow study of the rovibrational structure of molecules.

Great spectral purity is also needed for many experiments; the ratio of the third harmonic to the first, \( \frac{I_3}{I_0} \), must be less than \( 1 \times 10^{-5} \).

These requirements must be satisfied within certain practical constraints, many of which arise from the undulator.

**Bending Magnet Beamline.** Figure 5-3 shows a layout for the bending magnet beamline. The real image from the toroidal mirror (M1) is demagnified (in the vertical direction only) by a small spherical mirror (M2) to match the 20-mm slits that are required to get \( \Delta \lambda / \lambda = 1/50,000 \) with the proposed monochromator. The monochromator is assumed to have a 5-m-radius, 2400-lines/mm grating. The remaining two mirrors (M4 and M5) are required to deliver the beam to the desired delivery point at the proper height (six feet above the laboratory floor) and direction (horizontal). The fabrication tolerances required for the resolution-determining components—the grating and flat folding mirror—are about 1 \mu rad. This is challenging, but published spectra bear witness that it has been achieved. It is likely that the experimental station using this beamline will be located inside the ALS experimental area; this could result in a shorter, more efficient, and less technically challenging configuration than the beamline described in Fig. 5-3.

**Undulator Beamline.** The undulator beamline design, shown in Fig. 5-4, is based on similar requirements and uses essentially the same monochromator system as the bending magnet beamline. The main differences are due to the smaller divergence angle of the beam and its greater power. Consequently, there are two grazing-incidence mirrors, M1 and M2, whose role is partly to condense the beam onto the entrance slit and partly to absorb the large amount of power that will be present in the undulator beam at photon energies outside the range needed for this program. The monochromator for this beamline differs from that used for the bending magnet beamline only in the size of the displacement produced by the folding mirror M3.

The mirrors M1 and M2 and the normal-incidence mirror M3 absorb sufficient power that the grating G1 does not need to be water cooled. This allows both monochromators to be standard commercial items. A by-pass could be
Figure 5-3. Side view of the optical layout for an example beamline, designed for an ALS bending magnet.
Figure 5-4. Side view of the optical layout for an example beamline, designed for a U10.0 ALS undulator.
provided between M2 and M3 to accommodate experiments that require very high fluxes and for which high resolution is not critical. Options such as branch lines for deflecting the output from the monochromator to various experimental stations will be studied. Once again, the two condensing mirrors, M4 and M5, are needed to deliver the monochromatic beam to the sample at the proper height and direction.

**Output Flux and Geometry.** At the interaction region, the phase space of the photon beams provided by the two beamlines, when they are set for a slit-width-limited resolution of 0.016 Å with a 1200-lines/mm grating (10-μm slits), is as follows:

<table>
<thead>
<tr>
<th></th>
<th>Bending magnet</th>
<th>Undulator</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vertical:</td>
<td>0.90 x 12 mm-mrad</td>
<td>0.011 x 4.9 mm-mrad</td>
</tr>
<tr>
<td>Horizontal:</td>
<td>0.78 x 22 mm-mrad</td>
<td>0.1 x 2.8 mm-mrad</td>
</tr>
</tbody>
</table>

These figures are the Gaussian optics values, which are expected to be good in general, but in some cases, the astigmatic focal line length may be larger than the quoted horizontal spot size. This can be corrected if it is considered important. The effects of optical fabrication tolerances and aberrations have not been allowed for, and they might be expected to produce some degradation in the quoted values of the vertical spot size.

For the photon fluxes emitted by the two ALS sources, the output does not vary greatly over the spectral range involved in this work. The same is roughly true for the reflecting efficiency of the carbon and silicon carbide coatings proposed. It is therefore reasonable to quote a single figure for the photon flux expected from each of the two beamlines. For the optical systems described here, with the ALS operating at 400 mA and 1.5 GeV, we obtain (for energies between 6 and 30 eV):

- Undulator beamline, $\Delta \lambda/\lambda = 1/50,000$ \quad $3 \times 10^{11}$ photons/s
- Undulator beamline, $\Delta \lambda/\lambda = 1/44$ \quad $3 \times 10^{14}$ photons/s
- Bending magnet beamline, $\Delta \lambda/\lambda = 1/50,000$ \quad $1 \times 10^{10}$ photons/s

The flux is higher by as much as an order of magnitude for the by-pass option of the undulator beamline.

**Higher-Order Suppression.** It is essential for applications at the CDRL that higher diffracted orders be less than $10^{-5}$ times the intensity of the first order. The
problem is particularly serious for the spectral region of interest here, because, at the ALS electron energy, undulators must be operated at high magnetic fields to generate low-energy photons in the first harmonic. As a consequence, the higher-order radiation is generally more intense than is the desired radiation. A similar argument applies to the bending magnet source, which also produces more higher-order than first-order radiation, because of the value of the ALS critical energy (1.56 keV). We have made the best possible use of the optical factors that can be used to discriminate against higher orders; that is, reflection filtering and use of a laminar grating with a mark-to-space ratio of unity. This is quite effective near the normal-incidence reflectance threshold of the silicon carbide reflection surfaces that are used on all the optical components. However, it becomes ineffective at wavelengths greater than twice the threshold, where second and third orders may constitute as much as 10% of the total output. To obtain an improved rejection of the higher orders, absorption gas filters in a differentially pumped arrangement will be used. A system with the geometry shown in Fig. 5-5 transmits less than $10^{-6}$ of the incoming high-order photons, assuming the correct choice of gas for the prevailing spectral region. Typically, the absorber gas is one of the noble gases. For wavelengths longer than about 110 nm, crystalline windows are very effective for higher-mode suppression.

![Figure 5-5](image.png)

**Figure 5-5.** Schematic drawing of a proposed gas filter for reducing the transmission of higher-order radiation in the ALS bending magnet and U10.0 beamlines.
5. FACILITIES

5.1.3 Advanced Laser Systems at the CDRL

Some of the lasers needed for the CDRL are fairly standard "off the shelf hardware" and, to a substantial degree, can be purchased commercially and used without modification. A number of lasers that fall into this category are mentioned in Section 3, in connection with the research programs that will require them. However, some experiments will also need laser systems whose performance and sophistication surpass the state of the art of commercial systems available from any single manufacturer. The preliminary specifications given for these systems are based on performance reported by researchers in various development laboratories. The final performance specifications will be developed and refined in workshops before CDRL construction begins.

These advanced lasers will be very substantial in size; they will remain stationary in the experimental hall of the CDRL, and their output will be transported to the end station as required, in contrast to standard lasers, which could be moved to a location close to each experiment, as needed.

Two advanced laser systems are described in the following paragraphs.

Near-Transform-Limited Tunable Laser System. A near-transform-limited source operating in the nanosecond regime will provide high-power, tunable photons from 4 μm to 70 nm with exceptional frequency resolution. This laser, the IRFEL, and the ALS undulator beamline are all high-intensity sources, and they complement each other's spectral capabilities. Together, they provide complete coverage of the portion of the spectrum most important to chemical dynamics and combustion chemistry investigations. This laser can be synchronized to the macropulse timing of the IRFEL.

This system is an improved version of one that is in operation at LBL. It has a near-transform-limited bandwidth of <100 MHz in the visible region for a 7 ns (FWHM) pulse. It also has a high pulse energy, typically around 100 mJ in the visible and 30 mJ in the UV, with good beam quality; this allows efficient conversion into the VUV and XUV regions. With the use of frequency tripling and mixing techniques, it is continuously tunable over a broad range in the VUV and XUV, producing fluxes of >10^{11} photons/pulse in a bandwidth of 250 MHz (0.008 cm^{-1}). Difference frequency generation in LiNbO_{3} or LiIO_{3} extends the tunability to the IR. A total useful tuning range of 4 μm to 70 nm is expected. A schematic of the system is shown in Fig. 5-6.
Figure 5-6. Schematic of the near-transform-limited tunable laser system proposed for the CDRL.
5. FACILITIES

The basic technique used in the construction of this laser system is pulse-amplification of a single-mode dye laser. The system consists of two identical subsystems. In each subsystem, we start with a narrow-band cw ring dye laser (Coherent model 699-29 Autoscan ring dye laser), pumped by an argon ion laser. This gives a well-characterized light beam of 1 MHz bandwidth, continuously tunable over the whole visible spectrum. The pulses are then amplified by the second harmonic of a Nd:YAG laser, using a three-stage, four-pass dye amplifier chain similar to one that has been built at LBL. The dye laser is optically isolated from the amplifier chain with a permanent-magnet Faraday isolator to prevent mode-hopping induced by the feedback of amplified spontaneous emission from the amplifiers. The beam of pulsed visible photons is then sent through a frequency-doubling crystal, and the UV photons thus generated are used to make VUV and XUV radiation via third-harmonic generation or four-wave mixing in a pulsed atomic or molecular beam. Table 5-3 shows the performance of the present system. The new system is expected to meet or exceed these characteristics.

Table 5-3. Performance characteristics of the present LBL near-transform-limited laser system.

<table>
<thead>
<tr>
<th></th>
<th>Visible</th>
<th>UV</th>
<th>VUV-XUV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy</td>
<td>&gt;100 mJ</td>
<td>&gt;30 mJ</td>
<td>&gt;10^{11} photon/pulse(^a)</td>
</tr>
<tr>
<td>Bandwidth (FWHM)</td>
<td>91 MHz</td>
<td>&lt;140 MHz(^b)</td>
<td>250 MHz</td>
</tr>
<tr>
<td>Pulse length</td>
<td>7 ns</td>
<td>&lt;7 ns</td>
<td>&lt;7 ns</td>
</tr>
<tr>
<td>Present tuning range</td>
<td>548–680 nm</td>
<td>274–340 nm</td>
<td>70–170 nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>210–260 nm</td>
<td></td>
</tr>
<tr>
<td>Temporal profile</td>
<td>near-Gaussian</td>
<td>near-Gaussian</td>
<td>near-Gaussian</td>
</tr>
</tbody>
</table>

\(^a\)Measured at 98 nm  
\(^b\)Estimated
Facilities at the CDRL

**Picosecond Tunable Laser System.** A second system, operating either in the sub-picosecond regime or in the picosecond regime, will provide tunable photon pulses that are time-synchronized to the pulse trains from the ALS beamlines and from the IRFEL. These will be most suitable for pump-probe experiments involving the micropulses from the accelerator-based systems. This laser could be used with either the ALS beamline or the IRFEL at the micropulse repetition rate of 36.6 MHz. Another emphasis is to produce intense visible and UV pulses, synchronized with the macropulse timing of the IRFEL.

This system is similar in its basic engineering idea to the near-transform-limited laser system described above. *The system described here is based on proven current technology; the actual choice of components will be driven by the latest technological developments at the time of implementation.* It will have two dye laser oscillators, each followed by a high-power amplification stage and a nonlinear optical-wavelength-extension stage. The basic oscillator will be a mode-locked, frequency-doubled Nd:YAG laser, synchronously pumping a dual-jet dye laser, providing two independently tunable pulses in the 1-ps range. The significant part is that the mode-locked laser will be driven externally by RF at 36.56 MHz, derived from the ALS RF oscillator, thus synchronizing the dye laser pulses to the ALS and the IRFEL pulses to within a few picoseconds. The laser operating at this repetition rate will have low pulse energy (~1 nJ) and is functional in the visible. Infrared pulses from the mode-locked Nd:YAG laser will be regeneratively amplified and frequency doubled to yield several mJ/pulse at 532 nm. A double-pass dye amplification stage, with a cavity dumper in the dye laser, will provide up to 500 μJ of visible energy in the picosecond pulse. At this power level, frequency doubling and mixing are efficient and will permit extension of the wavelengths into the UV and IR. "Multicolor" experiments requiring three and even four different wavelengths at high repetition rates can be planned, involving the ALS, IRFEL, and these dye lasers. A schematic of the system is shown in Fig. 5-7.

5.1.4 Experimental Stations at the CDRL

Central to the utility of the CDRL are the experimental stations where beams from the facility's various photon sources converge to allow new and unique experiments to be performed. These stations will be fully equipped with molecular beam apparatus, beam sources, apparatus for kinetics studies, ultrahigh-vacuum apparatus, conventional laser systems, and automated data acquisition and control systems.
Figure 5-7. Schematic of the picosecond laser system proposed for the CDRL.
Because of the breadth and complexity of the potential CDRL research program, the exact configuration of the experimental stations will be determined by the users' needs. Details of the stations will evolve and be refined through continuing planning and discussion among the core research groups and the participating user groups, and in scientific and technical workshops to be held before operations begin. Responsibility for reviewing the proposals that emerge from these discussions and for establishing construction priorities rests with the Program Review Panel, as outlined in Appendix B.

Nonetheless, many general principles and guidelines can be laid out now, and the large end-station apparatus and special lasers must be designed in advance.

The main components that distinguish one experimental station from another are the vacuum chambers for beam experiments, or sample cells for bulk experiments, and their peripherals. Each chamber or cell is designed for a specific class of experiments. Each will be designed so that attachments such as beam sources, detectors, and window flanges can be fitted universally to many of the main chambers. Each station will be equipped with data acquisition capability to take full advantage of the unique research facilities. It will also be equipped with state-of-the-art photolysis lasers and probe lasers as needed, in addition to the advanced lasers described above. These lasers and electronics will be shared among the stations.

To prevent accidental contamination of the beamline optics and expensive components in the storage ring of the ALS, oil-free pumping systems will be employed wherever possible. A network of vacuum forelines is designed for the experimental hall, with the roughing pumps located in the basement of the building to maintain cleanliness and reduce the noise level in the hall.

General descriptions of several experimental chambers and conventional lasers, suggested by the needs of workers in different areas of research, can be found in Section 3.

5.1.5 Computational Facility

Highly productive research will require broad and vigorous interaction among theorists and experimentalists. The CDRL will provide a supportive environment for this interaction. The computational facility of the CDRL will be located on the third floor of the CDRL building. Two forms of computing capabilities will be provided. First, several state-of-the-art workstations, each with a minimum of 10–15 megaflops, 128 megabytes of memory, and 1 gigabyte of storage,
and/or a super-minicomputer, will be located in a centralized, environmentally controlled room. They can be accessed with terminals via Ethernet or a fiber optics network throughout the building. This local-area network will also be connected to the ALS and other parts of LBL for efficient communications. Second, a 1.5-megabit communications link between the CDRL building and the SNL central computer facility will allow high-speed access to a DOE supercomputing facility for computations that require very "high-horsepower" resources. A schematic layout of the communications links is shown in Fig. 5-8a.

These capabilities will be available for various computations, including the development of new theoretical methods for efficient and reliable treatment of molecular collision dynamics and intramolecular processes, exact three-dimensional quantum scattering calculations, accurate ab initio calculations of potential energy surfaces, and development of new methods to determine rovibrational eigenvalues. High-speed links to the UC Berkeley campus and video conferencing facilities between the CDRL and SNL will also be installed.

![Figure 5-8. (a) Schematic layout of the computational facilities at the CDRL; LAN, local area network.](image-url)
To enhance the interaction among theorists and experimentalists, offices in the third floor of the laboratory building will be occupied by 5 in-house and 5-10 visiting theoretical chemists, in close proximity to the experimental effort. As part of the activities of the computational facility, weekly seminars and an annual workshop will be held. The fellows program described in Section 4.3 will help in attracting outstanding theorists to participate in the programs of the laboratory.

5.2 FACILITIES AT THE CRF AND CCCS

5.2.1 Center for Computational Combustion Science

Theory and modeling play significant roles in advancing fundamental knowledge in combustion science and chemical physics. Progress in these areas has depended traditionally on the availability of state-of-the-art computing resources. This section describes how this capability will be provided for in-house and visiting researchers at the CCCS. The long-term focus of the CCCS will be to develop

![Diagram of computational facilities]

Figure 5-8. (b) Schematic layout of the computational facilities at Sandia National Laboratories–Livermore (SNLL).
predictive combustion models that incorporate the theoretical and experimental understanding of fundamental processes derived from basic and applied research activities at the CDRL and the CRF. Elements of these processes include the energetics of molecules and radicals, the kinetics and dynamics of chemical reactions, turbulent fluid motions, and heat and mass transfer.

Major challenges exist in providing theorists and modelers with computer resources. One is that computer technology is evolving at a tremendous pace. Supercomputers costing millions of dollars are rendered obsolete in just a few years. Furthermore, it is widely believed that massively parallel computers, based on thousands or even tens of thousands of inexpensive processors, will provide the only long-term avenue to attain the speedups needed to develop predictive capability in many areas, including combustion. However, in addition to evolving rapidly, these massively parallel computers have the added complication of being extremely difficult to program. Currently, significant computations are usually accomplished only with the assistance of computer scientists.

Computational Resources. Responding to these challenges, the CCCS approach differs from those of comparable research centers in one important respect. Rather than acquiring a single, expensive mainframe computer, the CCCS will emphasize the solution of computational problems by using the best available computer technology, whether it be supercomputers or massively parallel computers. Through the planned operating budget of the CCCS, computer time will be purchased on a variety of computer systems. For traditional supercomputer access, the time will be purchased on a Cray-class machine located within the SNL computer center. For massively parallel computing, commercially available time will be purchased. Although the CCCS will not become operational for several years, commercial availability of massively parallel computer has been assessed. If the CCCS were to become operational immediately, significant time could be acquired on a 1024-processor N-Cube and a 65,536-processor Connection Machine. Both of these architectures have demonstrated capability in solving practical computational problems. It is anticipated that commercial sources of massively parallel computer time will continue to be available in the future.

Computing Environment. As with experimental capabilities, support for visitors will be a primary focus of the computational portion of the CCCS. To utilize these resources effectively, a computing environment will be provided that supports high-speed (at least 1-Mb) networking (see Fig. 5-8b). A separate building will accommodate in-house staff and up to 30 visitors simultaneously. Each office will support very high-speed access to the central computer network, and intersite
Facilities at the CRF and CCCS

(LBL/SNL) communications will provide access to personnel located at LBL. No off-site access (i.e., outside SNL and LBL) to the computer network is planned, consistent with the objective of providing computer resources to in-house and visiting scientists only.

To provide staff for supporting these computational activities, the CCCS budget contains two FTEs for programmer/analyst support and technical support to maintain and develop the network, as well as to support the use of scientific workstations.

5.2.2 Femtosecond Laser Facility

Figure 5-9 presents a layout for the femtosecond laser system proposed for the CRF. The source of ultrashort pulses will be a dye laser oscillator capable of producing 100-fs pulses, probably near 600 nm. The pump for this dye laser could be a cw argon laser or a mode-locked, frequency-doubled Nd:YAG laser. In the former case, pulses will be as short as 27 fs. In the latter case, 80-ps pulses at 532 nm or 1.06 μm will be available from the pump laser. In either case, pulses from the dye laser will have low energy (100 pJ), but a high repetition rate (100 MHz). Amplification of these pulses by a copper vapor laser-pumped dye amplifier will yield more energetic pulses (40 μJ), but at a lower repetition rate (5 kHz). A pulse compressor can then reduce the length of these pulses to ~10 fs with 15–20% energy efficiency. Finally, additional frequency-doubled Nd:YAG-pumped dye amplification can increase the pulse energy to ~1 mJ or more. At any stage, nonlinear optical crystals can shift the lightwave into the UV.

We will stress making this femtosecond technology readily accessible to combustion researchers. This objective coincides closely with that of the group at the Laboratoire d’Optique Appliquee, ENSTA, Ecole Polytechnique, in Palaiseau, France, where a femtosecond laser has been built with many ports available for visitors. While this French group has concentrated on condensed-phase studies, we will emphasize atomic and molecular studies relating to combustion and to materials in chemically reactive environments. Interest in these latter two research areas is high not only at SNL, but also at universities engaged in fundamental studies of energy-transfer processes. Since the CDF will be operated as a DOE user facility, access by university researchers to both the femtosecond laser system and the multiple-beam Nd:YAG/dye laser system will be strongly encouraged.
Femtosecond Facility Laser

- Highly versatile
  - Pulse lengths down to 10 fs
  - Wide range of energies and wavelengths
  - Multiple output ports

- Ultrafast processes
  - Unimolecular chemistry
  - Collision dynamics

- 3-Dimensional Imaging

- User-friendly

Figure 5-9. The proposed CRF femtosecond laser facility.
5.2.3 Multiple-Beam Nd:YAG/Dye Laser Facility

Three important constraints for laser systems used to study turbulent and transient reacting flows are tunability, energy, and repetition rate. To perform fluorescence imaging, much of the visible spectrum must be accessible, and to perform Raman imaging, outputs on the order of joules must be available, even at wavelengths near 440 nm. The best candidates for meeting these requirements are dye lasers, which deliver the highest energy output over the widest frequency range.

The multiple-beam laser for the CRF will consist of ten frequency-doubled, Q-switched Nd:YAG lasers, each pumping its own dye laser. This design will allow investigators to obtain ten images at repetition rates up to the inverse of the laser pulse width. To provide maximum flexibility, the facility will provide 532-nm output, tunable narrow-band dye laser output, broad-band dye laser output, or combinations of these, depending upon the requirements of the experiments. The dye lasers can all be operated at the same wavelength or at different wavelengths. Thus, the multiplexed laser arrangement will provide a powerful, versatile laser system capable of producing a train of laser pulses with arbitrary timing and nearly arbitrary wavelength. A control computer will allow programming of the firing sequence, flashlamp energy, and other operational parameters, and will provide data acquisition and control of laser beam diagnostics. A summary of the performance specifications of the multiple-beam Nd:YAG/dye laser system is given in Table 5-4.

The beam multiplexing scheme for combining the beams is illustrated in Figure 5-10. Two laser beams having mutually orthogonal polarizations can be spatially superimposed with a polarizing beamsplitter. Because the two lasers will be fired sequentially, not simultaneously, a Pockels cell placed after the beam-combining polarizer can be used to rotate the polarization of one of the beams (by applying the half-wave voltage) to match the polarization of the other beam. This matching allows many stages to be cascaded to combine an arbitrary number of individual laser users.

The major technical challenge in designing and building the multiple-beam laser system is combining the beams. The beam-multiplexing scheme described above is now technologically feasible. Pockels cells with 2–3% optical loss are available, as are polarizers and half-wave plates with low-loss, antireflection coatings. Thus, the technology exists for combining many laser beams. The task of combining ten laser beams is, nevertheless, not trivial. The beam-combining hardware must permit several wavelengths to be transmitted efficiently, a difficult
requirement if the wavelengths are not almost the same. In CARS applications, for example, a portion of the 532-nm Nd:YAG beam must be split off and transmitted with the dye laser beam. This will require a parallel network or tree structure of Pockels cells for the 532-nm beam. The performance of the beam-combining technique for a two-beam system is now being evaluated. Since the approach is modular, scaling from a two-beam to a ten-beam system will be straightforward.

Table 5-4. Specifications for the CRF multiple-beam Nd:YAG/dye laser system.

*Fast-Frame-Rate Imaging Mode*

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Single pulse energy (mJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1064</td>
<td>740</td>
</tr>
<tr>
<td>532</td>
<td>350</td>
</tr>
<tr>
<td>355</td>
<td>150</td>
</tr>
</tbody>
</table>

Repetition rate (Hz): 100–200 maximum
Framing rate (MHz): 100 maximum

*Bunched-Pulse Mode*

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Single pulse energy (mJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1064</td>
<td>7400</td>
</tr>
<tr>
<td>532</td>
<td>3500</td>
</tr>
<tr>
<td>355</td>
<td>1500</td>
</tr>
</tbody>
</table>

Repetition rate (Hz): 10–20
Multiple-beam Nd:YAG/Dye Facility Laser

- User friendly
- Combustion imaging applications
- Fast-frame-rate imaging mode
  - Framing rates up to 100 MHz
  - Ten consecutive single-shot images
  - Repetition rates up to 100 Hz
- Bunched-pulse mode
  - Raman imaging
  - Low-noise broadband CARS
- State-selective chemical dynamics

Figure 5-10. Schematic of the multiple-beam Nd:YAG/dye laser proposed for the CRF.
APPENDIX A. CDF STEERING COMMITTEE CHARTER

I. Function and Reporting

The Combustion Dynamics Facility (CDF) Steering Committee is appointed jointly by the Lawrence Berkeley Laboratory (LBL) Director and the Sandia National Laboratory (SNL) President to provide advice on major policy issues that bear on effective utilization of the CDF. The Committee serves two primary functions:

• To advise SNL and LBL on policy aspects of CDF development, operation, and plans for the future; and

• To ensure that the CDF operates as a national facility whose development and utilization contribute maximally to scientific and technical productivity.

In providing this advice, the Committee will consider the quality of the science and/or technology that will result from the CDF program, benefit to others in the combustion, chemistry, and technological communities in both the public and private sectors, and the mix and balance of programs and facilities among the in-house researchers, external users, and collaborations involving both internal and external users.

II. Membership

The CDF Steering Committee will be composed of nine persons appointed jointly by the LBL Director and SNL President, who are distinguished by excellence of scientific or technological accomplishment and experienced in the management of scientific organizations. Membership on the Committee will be for a three-year term, renewable for no more than one term. To ensure continuity, terms will be staggered; hence, initial terms will be of two, three, or four years duration until a proper rotation sequence is established.

III. Mode of Operation

The CDF Steering Committee will meet as often as necessary, but no less than annually.
APPENDIX B. CDF PROGRAM REVIEW PANEL CHARTER

I. Function and Reporting

The Combustion Dynamics Facility (CDF) Program Review Panel (PRP) is advisory to the LBL Director and the SNL President and will provide them, through the CDRL and CRF Directors, respectively, with specific recommendations on the disposition of all proposals for the development and use of CDF facilities of all types.

During construction of the CDF, the primary responsibility of the PRP will be to review proposals for CDF experimental stations and to review at six-month intervals progress toward implementation of the selected proposals. Criteria to be considered in the review of experimental station proposals include: uniqueness and quality of the proposed chemistry and/or combustion program, benefit to others in the chemistry and combustion communities, impact on other science and technology at the CDF, fiscal resources and personnel available for development of the proposed experimental station, and the ability of the proponents to carry out the proposed program successfully. The PRP will be assisted in this review by the CDF Staff. Criteria to be considered in the review of experimental station progress include timely achievement of milestones and adherence to the procedures outlined in the cover agreement that shall be executed between the proposers and the CDRL Director before final approval of a proposal.

The requested budget for the CDF includes funds for five experimental stations. Specifications for four of the stations will be developed incorporating user input; specifications for the remaining one will be developed by the in-house research group. For the user-specified stations, resources for design and construction will be awarded competitively, following review by the PRP. Two will be specified solely by external user groups; plans for the remaining two will be developed through collaborative proposals submitted by teams comprised of both in-house researchers and external users. Time for subsequent utilization of all of the stations will be available to in-house researchers and external users, consistent with the allocation guidelines defined in Section III. The PRP will also review periodically and make recommendations regarding the allocation of resources for the development of other experimental stations related to the CDF/ALS undulator and to the IRFEL.
During CDF operation, the PRP primarily will be responsible for reviewing research performance at the CDF, and for providing peer review of proposals for the use of research time on the experimental stations at LBL and SNL. During the conduct of this process, the PRP may impanel subcommittees and/or obtain outside referees for proposals before making recommendations to the CDRL and CRF Directors. Separate subcommittees may be needed for the CDRL and the CRF programs. After receipt of the PRP recommendations, the CDRL and CRF Directors will forward the recommendation on each proposal through the appropriate management chain to the LBL Director and the SNL President (or designee), who has final authority for acceptance or rejection of proposals.

II. Membership

The members and chair of the PRP will be appointed jointly by the LBL Director and the SNL President. The CDRL and CRF Directors will recommend nominees to the LBL Director and the SNL President after consultation with the CDF Steering Committee, LBL and SNL management, and with the external community. The PRP will consist of eleven members, including the CDRL and CRF Directors. Membership will be balanced to cover the major chemistry and combustion disciplines served by the CDF. No more than four members will be LBL or SNL staff.

Membership on the PRP will be for a three-year term, renewable for no more than one term. To ensure continuity terms will be staggered; hence, initial terms will be of one, two, or three years duration until a proper rotation sequence is established.

III. Mode of Operation

A. Procedures

All proposals to design, construct, and operate experimental facilities or to perform experiments on facilities of all types will be made available to the PRP. The distinctions between in-house, collaborative, and user experiments are discussed in Section III above. When the category of a proposal is unclear, the CDRL or CRF Director, after consultation with the chairperson of the PRP, will decide how a proposal is to be classified.

Regular progress reviews will be conducted during the design phase using procedures developed by the PRP in consultation with the CDRL and CRF Directors and staff.
B. Conflict of Interest

A member of the PRP will not take part in deliberations or votes when:

(1) His/her name appears in the proposal under consideration;

(2) Another proposal is being considered in direct competition with one in which the member is a collaborator; or

(3) His/her participation appears to create a conflict of interest.

C. Meetings

The PRP will meet as often as necessary but not less than twice a year. All proposals submitted at least two months before a given PRP meeting will be considered at that meeting.

The deliberations of the PRP will be confidential to the extent legally possible. The CDRL and CRF Directors, or their designees, will participate in the PRP deliberations as ex officio members except when the PRP chairperson determines a need for a private session.

D. Progress Reviews during the Operational Phase

After the CDF experimental facilities are operational, their utilization and appropriateness will be reviewed biannually by the PRP, which will make any recommendations it considers would improve the experimental program.
APPENDIX C: CDRL USERS’ ORGANIZATION DRAFT CHARTER

The purpose of the CDRL Users’ Organization at the Lawrence Berkeley Laboratory is to provide an organized framework for the interaction between those who use the CDRL facility for their research and the CDRL management, and to act as a participating research team (PRT) vis-à-vis the Advanced Light Source (ALS) synchrotron facility. The Users’ Organization, representing the researchers at the CDRL, will be in a position to make known to the CDRL management the needs and desires of the users regarding operating policy, the use of the CDRL, user support, and other relevant issues of concern. The Users’ Organization will help in developing user guidelines for the CDRL. It will also provide a mechanism for the CDRL management to inform users of current and future plans for the facility and to help in shaping these plans. The Users’ Organization, acting as an ALS PRT, will be responsible for interacting with the ALS management in conjunction with the CDRL management. Responsibility for the CDRL and the research program rests with the CDRL management. The role of the Users’ Organization shall be to advise the CDRL management on matters of concern to users.

I. Organization

A. Membership

Membership in the CDRL Users’ Organization shall be open to all those, including students, who are interested in the CDRL and who have used or plan to use the CDRL.

B. Executive Committee

The executive committee shall consist of five users who are elected for three-year terms by the CDRL Users’ Organization. The five members, who will represent both the theoretical and experimental programs of the CDRL, shall choose from among themselves a chairperson and vice-chairperson, each serving one year in that capacity, and with the vice-chairperson automatically succeeding the chairperson. A third person shall act as secretary.
II. Meetings

A. An annual meeting of the CDRL Users' Organization shall be called by the chairperson. The date of this meeting will typically coincide with the date of the ALS Users annual meeting.

B. The agenda or program for the meeting, established by the Executive Committee, shall be disseminated to the CDRL users at least two months in advance of the annual meeting.

C. The Executive Committee shall meet at the call of the chairperson to transact all such business as shall be required between each general meeting of the users.

III. Procedural Rules

A. Minutes of all meetings shall be recorded by the secretary and shall include a brief resume of the results of the deliberations. After approval by the chairperson, copies of the minutes of the meetings shall be provided to all CDRL users and the CDRL management.

B. Meetings of the CDRL Users' Organization or its Executive Committee shall abide by Robert's Rules of Order.

C. This Charter can be amended by a mail ballot of the members of the CDRL Users' Organization, conducted by the Users' Executive Committee. A two-thirds majority of those members voting in the balloting must vote in favor of an amendment for it to be adopted.

D. In the event that a position on the Users' Executive Committee should be vacated before expiration of its term, the Committee shall appoint a member of the Organization to fill the position for the duration of the unexpired term.

IV. Purpose of the Users' Organization

A. The Users' Executive Committee, acting on behalf of the Users' Organization, shall advise the CDRL management with regard to membership of relevant committees that may be established. The CDRL management shall keep the Users' Executive Committee advised of proposed changes in the operation of the CDRL. The Committee shall have responsibility for making appropriate recommendations to the CDRL management regarding such matters, including future directions, major equipment purchases, the management of the theoretical/computational aspects of the CDRL, and future user needs.
B. The Users’ Executive Committee shall act through its chairperson or his/her designee as the spokesperson for the users in all CDRL interactions with the ALS. This will include the preparation of progress reports and practical issues related to the beamlines.
APPENDIX D. CDF VISITORS PROGRAM COORDINATOR

The CDF Visitors Program Coordinator is responsible for developing and maintaining a strong visitors program at the CDF. In addition to aggressive recruitment of users, the CDF Program Coordinator advises the CDF Directors concerning requirements needed to ensure that the experimental facilities being developed and constructed within the constraints of the assigned CDF visitor resources are sufficient to carry out the scope of the anticipated research programs desired by the user community. Specific duties include:

- Represent the CDF to the scientific community by preparing papers and giving talks that address the scientific capabilities of the CDF and the major scientific opportunities within the CDF.

- Provide liaison to the user community. This includes working with the community to develop their suggestions and input for CDF research, for CDF experimental facilities, and for other issues that impact the scientific program and user environment at the CDF.

- Provide advice to the CDRL and CRF Directors concerning requirements for the optimal utilization of the facilities for first-rate scientific programs; with the CDRL and CRF Directors, provide input to the user community concerning the technical and resource constraints that may impact the scientific program or the environment for user activities.

- Consolidate various user groups with compatible research interests into teams to strengthen the resulting proposals and to maximize the number of users that can participate effectively in the development and use of experimental facilities. These teams may comprise solely external users or collaborations between visitors and in-house researchers.

- Provide staff support for the CDF Program Review Panel and, working with the Panel Chair, arrange meetings and assure that background information is provided to Panel members in a timely manner.

- Conduct and provide to the PRP and CDF Directors analyses of the initial proposals submitted by the user community. These analyses should address issues including the feasibility of the proposed program, the uniqueness of the
CDF as a source for the work, the ability of the proposing team to carry out the work effectively, and the impact on CDF resources if the proposal is approved.

- Work with the spokespersons for approved proposals to develop user agreements addressing the commitments and responsibilities of the CDF and of the user groups for successfully carrying out the approved research program.

- Assist the Directors in developing policies and procedures relevant to the operation of the CDF.
APPENDIX E. SCENARIO FOR THE
DEVELOPMENT AND EXECUTION OF A SCIENTIFIC PROJECT AT THE CDF

This document has identified three modes of conducting research at the CDF: the independent external user mode, the in-house mode, and the collaborative mode. To clarify the procedure for proposal development, we provide here a concrete example of how a project develops from conception as an idea to the successful completion of a research program at the CDF. The example shows how different parts of the CDF organization come into play during the proposed development. This example involves a collaborative-mode project, which is administratively the most complicated of the three modes. We assume that total funding support is required from the CDF and/or the DOE.

Professor User of General State University (GSU) and Professor Resident, a CDF principal investigator, discuss radical beam production and realize that IR multiphoton dissociation using the IRFEL may be an efficient way to produce an intense beam of cold vinyl radicals, an important but elusive combustion intermediate. They decide to collaborate on a proof-of-principle experiment to test the idea at the CDF where the IRFEL can be used for radical production and the ALS beam line can be used to detect radicals. Furthermore, if the experiment is successful, they plan a longer-term research program to study the reactions of vinyl radicals with various aliphatic and aromatic hydrocarbons using the universal crossed-molecular-beam method.

The first step is to obtain support for the short-term, proof-of-principle experiment. With the assistance of the visiting program coordinator and staff of the CDF, Professors User and Resident develop a short collaborative project proposal and submit it to the Program Review Panel of the CDF for consideration. The proposal briefly summarizes the underlying scientific idea, its significance and the approach. It contains a feasibility calculation, a list of facility requirements, and an estimate of required duration to carry out the experiment.

Since Professor User's students and postdocs are committed to projects at GSU, supported by other agencies, he additionally requests student/postdoc support by the CDF for the proof-of-principle experiment. Professor Resident's research is already supported through the DOE or other agency and is not eligible for additional
CDF funding. A budget is submitted for this purpose, indicating level of staffing cost and any other unusual research costs. Staffing cost pays for time spent by Professor User's research staff at the CDF. Unusual costs include for example, moderate modification of vacuum chambers and/or detection scheme, and expensive chemicals and optics. A separate request for housing and travel subsidy with justification is included. Professor User will be required to provide complete information on his research support.

This proposal is submitted at least two months prior to the meeting of the PRP. Upon receipt of the proposal, the CDF professional staff prepares a written comment on the feasibility and suitability of the project with respect to the facilities at the CDF. The CDF director indicates to the PRP if sufficient funds are available to cover the estimated research cost. The PRP then judges the proposal solely on its scientific merit. It prioritizes it along with all other proposals received and recommends the allocation of IRFEL time and ALS time (in this case simultaneously) to the project for the next scheduling period. Each scheduling period is for six months starting two months after the PRP meets. When approved, Professors User's and Resident's project will start some time during that scheduling period. The exact time slot is determined by the CDF director with assistance from his staff. Since the project does not require special timing (filling pattern) of the ALS, the ALS is notified to ensure compatibility but no special request to the ALS scheduling is needed. Under normal circumstances, Professors User and Resident will start their experiment four to ten months after submission of the proposal. If the experiment is not completed in the approved period, a new request is required with progressively diminishing probability of approval unless there is strong scientific justification.

When an exact time slot has been allocated, the Visitors Program Coordinator contacts Professor User to make plans for the stay of his research team member(s) at the CDF. Housing and transportation details will be arranged. Professional staff start to work with the research team to prepare details of arranging the experimental hardware and development of data-acquisition software. If this is Professor User's first visit to the facility, his research staff will enroll in an initiation class which covers the facility operation and safety features. Professor Resident's staff works at the CDF and will be proficient in using the facility. For the duration of the experiment, the professional and technical staff at the CDF will be available for consultation and assistance. The research team interacts closely with the IRFEL staff and the ALS staff to facilitate data acquisition.

Obtaining long-term support of the project that follows successful completion of the proof-of-principle experiment requires substantial lead-time. At the time
Professors User and Resident approach the CDF for time to perform their proof-of-principle experiment, they submit a Field Task Proposal (FTP/A) to the DOE Chemical Sciences Division for support of their long-term collaboration to study the chemical reactivity of radicals in beams. The FTP/A process takes roughly 18 months. If funded, it provides research personnel support for both Professor User and Professor Resident for the duration of the project. A few months before this funding begins, the team will request time on the CDF facilities. The request is similar to the proof-of-principle case except that no special financial assistance will be required. The PRP's purpose in this case is to determine the priority of this project relative to other requests. When it is appropriate, Professors User and Resident may approach funding agencies other than the Division of Chemical Sciences (DCS) for support.

At the conclusion of the project, Professor User's research team organizes the data and returns to GSU to interpret it. Professors User and Resident are required to file a report within three months, contribute to the CDF annual report, and may be required to give an oral presentation at the annual workshop/review of the CDF. Typically one or more scientific publication(s) in refereed journals is expected from a successful run. A new request is submitted to the CDF for follow-up experiments.

The scenario for external users follows closely that of Professor User. Core research has on-going financial support from DCS so that only the scientific case needs to be made to the CDF for time. On average, the 2:1:2 pattern for time utilization of the facilities will be adhered to by the PRP and the CDF.
APPENDIX F. CDF FELLOWS PROGRAM

I. Introduction

A Fellows Program will be established to facilitate extended visits by scientists from other institutions to join in the research programs of the CDF. Intended primarily for university researchers, tenure is from three months to one year. Fellowships are awarded competitively, as described below. This program is not envisioned to provide full salary support for visitors. Rather, it is intended to provide partial salary and supplemental living support—consistent with sabbatical-like arrangements—for visitors while in residence at the CDF. Based on experiences with similar programs in other institutions, it is anticipated that the CDRL will host four to eight fellows each year.

II. Mode of Operation

A. Announcement and Application Process

In July of each year, the CDF will solicit applications to the Fellows Program on an international basis through announcements in scientific news journals and mailings to university research departments. Interested scientists may obtain application forms from the CDF Visitors Program Coordinator; completed applications, including a brief description of proposed research, must be submitted by October 1. Applicants will be required to submit a brief financial statement; this information will be held in the strictest confidence.

B. Award Process

The first step in the award process will be a review by CDF management to screen out applications that clearly are inappropriate or beyond the scope of the CDF. Such applications will be returned to the submitter along with a letter of explanation.

Following the screening process, the proposals will be reviewed and ranked by the CDRL director in conjunction with the PRP in November of each year, based on the scientific qualifications of the applicant and the relevance of the proposed work to the CDF mission.
Independent of the scientific review process, administrative staff within the CDRL will determine the cost associated with each proposal. Typically this will include living expenses such as partial salary support, relocation expenses, and local living subsidies.

In early December, the CDRL director will make a preliminary selection, based on the scientific rank and the costs provided by the administrative staff. Typically, the selection process will involve funding the highest-ranked proposals, within the constraints of available funding. Final award letters will be mailed by the LBL director by the end of December. In the event that awardees decline, laboratory management will select the next-highest-ranked proposals, subject to available funding.

III. Review Procedures

The Fellows Program will be reviewed annually by the CDF Steering Committee. Criteria to be used in the review process include quality and appropriateness of the research, with regard to impact in basic science and effective use of unique CDF capabilities. In this capacity, the Steering Committee will advise the LBL director regarding the overall effectiveness of the Fellows Program. Laboratory and CDF management will use this information to maintain the health of the program and to guide changes where appropriate.
APPENDIX G. VISITOR ACCOMMODATIONS

Market Surveys. Conducted by the User Coordination Office of the ALS, these surveys have identified a reasonable supply of both short- and long-term housing in the Berkeley area. For example, the UC Faculty/Staff Housing Service maintains between 600-1,300 listings/month for units ranging from $310 (room) to $1,510 (4-bedroom house), monthly. Visitors will be assisted by CDRL administrative support staff and the ALS User Office in securing appropriate long-term housing. Short-term visitors will have a number of options. During the summer (June 1 – August 15) UC dormitories will be available to summer sabbatical professors and their students. Bed and Breakfast International, Inc., has a good reputation among visitors to LBL. In addition to obtaining the assistance of the User Office for the ALS in providing current information to all CDRL users in securing convenient housing, CDRL staff will continue to explore additional means of providing affordable housing.

Dedicated Housing. LBL has solicited proposals from the private sector to provide available dedicated housing for use by ALS visitors. As a result of this solicitation, the Durant Hotel is converting hotel space to dormitory-style space to be made available to LBL guests. If demand warrants, the Durant Hotel will convert additional floors. At Sandia, leased, furnished apartments are provided to users on a cost-recovery, first-come, first-served basis. Although contractual constraints preclude LBL from offering this service directly, provisions will be made, subject to approval by the DOE and the University of California, to extend this housing service to include units in the Berkeley area for CDRL visitors.

Related to housing is transportation and parking. Downtown Berkeley and the UC Berkeley Campus are served by rapid transit and buses, and there is a shuttle bus that operates every ten minutes during normal business hours. The shuttle bus schedule will be extended in 1992 when the ALS begins operation on a three-shift-per-day basis. A 1,000-car parking structure is being planned for LBL using third-party financing for those who elect to drive to LBL. The first 200 parking spaces are planned to be available in 1995, the earliest date that the CDRL will be operational.
APPENDIX H. CONVENTIONAL FACILITIES

I. The CDRL Building at LBL

The CDRL will be located in a new building directly adjacent to the ALS. Approximately 46,600 gross square feet in size, the three-story, braced-steel-frame structure with full basement will replace an inefficient and substandard existing building. The facility design includes a large heavy-laboratory experimental hall, eight support laboratories, and approximately 40 offices for researchers and visiting scientists. Figure G-1 shows the location of the building on the LBL site.

The high-bay experimental hall will be equipped with a 5-ton crane and is contiguous to the ALS experimental area. A support laboratory, a control room, and offices are located on the first floor, along with the experimental hall. The second floor is occupied by six support laboratories and offices, and the third floor is dedicated to offices and to computer, conference, and seminar rooms. The basement houses the IRFEL in a shielded vault, the mechanical pumps used for the experimental stations, and the mechanical and electrical equipment needed to support the research and the building. The IRFEL vault will be equipped with a 5-ton hoist.

The laboratory areas were designed to comply with H-7 occupancy requirements, and all code-stipulated mitigation measures for handling and storage of hazardous materials have been incorporated.

The HVAC system features a separate zone with 100% outside air supply for the experimental hall and each laboratory. An energy-efficient variable-air-volume system is proposed for offices and other support spaces. Mechanical equipment will occupy the basement and the interstitial space above the first floor and will be mounted on isolators and/or inertia blocks to minimize vibrational impact on the structure. Laboratories and the experimental hall will be equipped with fume hoods; vented chemical storage cabinets; house vacuum, liquid nitrogen, natural gas, compressed air, deionized water, low-conductivity water, industrial water, and acid drain systems.

The building will be served by a 5500-kVA dedicated electrical substation located in the basement. A 300-kVA emergency generator will be located on a pad.
Figure G-1. Site plan showing the location of the CDRL building.
outside the building. The building will also be served by 480/277-V and 208/120-V distribution systems with panel boards, branch circuit panels, and step-down transformers located in dedicated electrical rooms on each floor. The building will be equipped with telephone, communications, and fiber optic data circuits. Lighting controls will be zoned and automated, and integrated with the Energy Management and Control System.

Architecturally, the three-story building mass is modulated by the terracing of the upper floors. The exterior finishes of preformed metal siding, extruded aluminum windows, and heat-absorbing tinted glass were chosen to be compatible with and to complement the ALS Building exterior treatment, which in turn matches the finishes and proportions of the original, historically significant 184-Inch Synchrocyclotron Building.

II. Extension of the CRF at SNL

The extension of Sandia’s CRF will add approximately 32,300 gross square feet to the existing 51,000-square-foot multibuilding facility. The extension will add 21,200 square feet to the existing 16,400-square-foot laboratory building and 11,100 square feet to the existing 25,000-square-foot office building.

The laboratory building addition will be an L-shaped extension to the south and east of the existing building. Construction of the addition will match the existing building in architectural style, materials, and finishes; color; and floor-to-floor heights. The structure of the building will be steel framed, with precast exterior concrete shear walls (insulated), slab-on-grade floors designed for dampening and vibration isolation, a steel-framed louver-enclosed mechanical loft above the laboratories with metal and concrete deck (insulated), and a loft roof consisting of built-up roofing on metal decking. The laboratory building addition will provide 16 new laboratory spaces and 2 facility laser laboratories. The new facility laser rooms will be connected to serve any laboratory in the facility, via the Laser Duct and Periscope System. Laboratory spaces of varied sizes are planned to provide optimum flexibility of spaces, as required to operate the various experiments intended for the CRF. Free-standing acoustical partitions along the main corridor will enclose some work spaces, accommodating remote data acquisition and control equipment outside the laboratories.

Once-through conditioned ventilation will be provided from existing building fans for existing and new laboratory spaces to carry off fuel gases or vapors
and products of combustion, with systems included to minimize the discharge of contaminants to the atmosphere. An electronic safety monitoring and control system will provide back-up to the ventilation system.

Recirculated conditioned ventilation will be provided from a new fan system to the corridor and work spaces outside the laboratories, in both the existing building and the new addition. The existing system of ducts used for diagnostic laser beam transmission from the central laser rooms will be extended to all new laboratories. Other existing building systems such as power distribution, lighting, communications, security alarms, fire and evacuation alarms, automatic fire sprinkler, and piping and plumbing will also be extended to the addition.

The office building addition will provide space for 34 new offices, an open-office secretarial and file area, computer terminal rooms, and conference rooms. The addition will be a two-story wing added to the north of the existing office building and will match it in architectural style, materials and finishers; color; and floor-to-floor height. It will consist of a steel-framed structure with metal panel curtain walls, slab-on-grade floors at the ground level, second floor cellular metal decking with concrete fill, and an insulated metal deck roof with built-up roofing. Roof-mounted air-handling equipment will provide heating, ventilating, and air conditioning. An automatic sprinkler system, general and emergency lighting, electrical power distribution, communication systems, intrusion alarms, and fire and evacuation alarms will be provided.

III. The CCCS Building at SNL

The CCCS building will be an office-type building of approximately 30,000 gross square feet, adjacent to the existing CRF at SNL. The building will provide space for new offices, open-office secretarial and file areas, computer terminal rooms, and conference rooms. The CCCS will be of two stories, located southwest of the existing office building and will match it in architectural style, materials and finishes; color; and floor-to-floor height. It will consist of a steel-framed structure with metal panel curtain walls, slab-on-grade floors at the ground level, second floor cellular metal decking with concrete fill, and an insulated metal deck roof with built-up roofing. Roof-mounted air-handling equipment will provide heating, ventilating, and air conditioning. An automatic sprinkler system, general and emergency lighting, electrical power distribution, communication systems, intrusion alarms, and fire alarms will be provided.
Existing site utilities such as domestic and fire protection, water, sanitary sewer, natural gas, site lighting, and electrical power and special systems will be modified and extended to service this facility. An additional electrical substation will be provided. The roof penthouse will house a chiller, boiler, cooling tower, pumps, and controls.

The building will have provisions for heavy use of computer terminals and networks, but will not have provisions for main computers.