Chapter 1

Introduction

Structural dynamics is a very important process involving atomic motions, embodied in dynamical structural changes. It happens in all chemical and biological reactions, and many physical phase transitions. These structural changes span a wide time range, from femtoseconds (fs) to seconds or even longer. For example, the timescale of molecular vibrations is $\sim$100 fs and the timescale of molecular rotations is from picosecond (ps) to nanosecond (ns) [1]. In liquids, collisions of molecules happen in $\sim$1 to 100 fs. In solids, long-wavelength acoustic vibrations can persist for seconds or longer, but oscillations with wavelength at the atomic scale relax in a few picosecond or less. Some biochemical processes, such as conformational changes and local structural changes induced by ligand binding, occur on a fs timescale after external triggering. Within a protein, mechanical perturbations are essentially localized in $\sim$100 fs; acoustic dispersion takes place in the ps time range. To understand the mechanism of chemical and biological reactions and physical phase transitions stated above, it is ideal to follow the motion of atoms and identify the intermediate structures as the reactions and phase transitions proceed. As fundamental molecular vibrations and rotations happen in timescale about 100 fs, which corresponds to a distance of a few Å that the atomic nuclei travel, femtosecond and sub-ångström are the ultimate resolution in time and space needed.

Since the first laser realization in 1960, time-resolved experiments have advanced from nanoseconds to attoseconds, thanks to the generation of shorter and shorter pulses. In the last 15 years, with the discovery of fs pulse generation from solid state Ti-sapphire lasers, femtosecond lasers have become a standard laboratory tool. Femtosecond spectroscopy experiments provided not only better time resolution, but more importantly, new concepts and new phenomena [1]. Slower processes with characteristic times of nanoseconds or longer are governed by random diffusion of atoms and molecules. On the other hand, on the fs timescale, the coherent nuclear motions of nonequilibrium dynamics are observed. For complex processes, simpler events are resolved and transition states are trapped before thermal fluctuations blur the dynamical picture.

By using the fs pulses as a spectroscopic probe, with light wavelengths ranging from the ultraviolet to the infrared and terahertz, or other emissions such as electrons and ions, a great number of systems and processes in biology, chemistry and physics have been studied. The experiments can probe the evolution of the excited electronic states, such as carrier dynamics in metals and semiconductors, electron transfer in breaking and forming chemical bonds, and charge separation in photosynthetic reactions. But when the process under study involves structural change, only indirect structural information can be obtained, for example from frequencies of nuclear vibrations measured by infrared (IR) or Raman spectroscopy [2].

On the other hand, static structures with resolution much less than 1 Å are now routinely solved by diffraction methods [3]. X-rays, high energy electrons and neutrons are common sources to use in diffraction experiments. They have wavelengths comparable to the atomic spacing, and are scattered by the atoms to form diffraction patterns in the far field. In theory, the diffraction pattern is the Fourier transform of the atomic structure in real space. By inverse Fourier transform, the structure can be solved from the diffraction pattern. However, only the intensity of the diffraction pattern is detected in general diffraction experiments, whereas the phase of the diffracted beam cannot be recovered. Therefore more complex mathematical methods are needed to solve the complete atomic structures, such as phase retrieve algorithm and direct methods. In crystal diffraction experiments, molecules arrange in an ordered state in crystals and the repeated units give rise to distinct spots in the diffraction patterns, which makes it easier and more accurate to solve the atomic structures.

It is natural to see if one can combine the femtosecond time resolution of the ultrafast experiments and the sub-ångström spacial resolution of the diffraction techniques to study the structural dynamics directly. In femtosecond spectroscopy experiments, one general method is the pump-probe configuration. As in a movie, a continuous motion can be broken up into frames and captured with a brief exposure time. In the pump-probe femtosecond spectroscopy experiments, a femtosecond laser pump pulse initiates the process under investigation, and defines an exact time zero, t_0. Then another femtosecond laser pulse with different wavelength is used as a probe pulse, which arrives at the sample at some later point in time and provides a snapshot of the status of the process at that time. A full sequence of the dynamical process is achieved by using a precisely timed series of these probe pulses. And the individual snapshots combine to produce a complete picture of the continuous time evolution. For ultrafast diffraction experiment, the same method can be used only with a pulsed diffraction source as the probe.

Within the common sources used in the diffraction experiments, X-rays have wavelengths from 2.28 to 0.71 Å with an X-ray tube, and sub eV up to the MeV range with synchrotron radiation. The high energy electrons used in transmission electron microscopy have energies mostly in the range of 100 to 400 keV; with high voltage electron microscopes this range extends to 1 MeV or more. The neutrons used are usually the thermal neutrons from nuclear reactors with average energy $\sim$0.025 eV and corresponding wavelength $\sim$1.5 Å [3]. X-rays are scattered mostly by the electrons of the atoms, and the diffraction patterns are given by the Fourier transform of the total distribution of electrons. Electrons are scattered by both the electrons and the nucleus of the atoms, or by the potential field of the atoms, so the scattering amplitude is much larger for electrons, six orders of magnitude larger compared to that of X-rays. Neutrons are scattered by nucleus. Although the scattering amplitude for neutrons is small compared to both X-rays and electrons, it doesnot vary much with atomic weight. This makes neutrons attractive in detecting the positions of light elements, such as hydrogen, in the structure.

All three sources have been used in time-resolved experiments [4]. Especially for the X-rays from synchrotron radiation and the neutrons from the nuclear reactor, the sources are pulsed with pulse duration of nanoseconds. However, only X-rays and electrons have been used for ultrafast diffraction. For recent reviews, see reference [5] for ultrafast X-ray diffraction, and references [6, 7, 8] for ultrafast electron diffraction. Because of the aforementioned larger scattering amplitude, electrons are more sensitive for low density and low dimensional matters, such as gas-phase samples and surfaces. Also, electrons penetrate less and better match the optical penetration depth in most samples. On the other hand, electrons are less damaging to samples for the same diffraction signals (scattering events), especially for biological specimens. The technology for generating, deflecting and focusing the electrons is well developed and allows for "table-top" ultrafast diffraction and imaging experiments. For ultrafast X-ray diffractions, the laboratory size apparatus generates few photons for the diffraction experiments. In contrast, free electron laser (FEL) is very promising, only with very complicated and involved synchrotron technology and the construction is still in progress. There are challenges for ultrafast electron diffraction as well. Space-charge effect in nonrelativistic electron beams limits the electron numbers in the ultrashort pulses and accurate timing on fs timescales can be difficult. However, recent development of single electron diffraction and imaging technique can overcome the space-charge effect and reach fs time resolution [9].

Ultrafast electron diffraction (UED) for gas phase materials has been developed in the Zewail lab at Caltech since the early 1990s and reported on by others [10, 11, 12, 13]. In UED, the ultrafast electron pulses are generated by femtosecond laser pulses through photoelectric effect, and have pulse widths typically in ps with a few thousand electrons per pulse. Because of the homogeneous nature of the gas phase material, the diffraction patterns are composed of concentric rings. The interference is from different atoms in the gas molecules, and the molecular structure (bond distances and angles) can be solved by fitting the one-dimensional curve, which is obtained from radially averaging the diffraction rings. Due to the low density of the gas molecules, the diffraction signals are weak, and the diffraction from the transient species are even weaker. With tremendous efforts from the researchers here at Caltech, the sensitivity of the UED apparatus is now much improved to allow for the studies of molecules even without heavy atoms [12, 13]. The theoretical analysis and calculations are also highly advanced for better determinations of transient structures, even for complicated large molecules, and for coupling to complex reaction pathways [14, 15, 16]. A number of important photochemical and photophysical problems have been studied, such as the nonconcerted elimination of iodine atoms from $C_2F_4I_2$ [17, 18], the ring opening of cyclohexadiene (C_6H_8) [18, 19] and the ultraviolet excitation of acetylacetone [20, 21]. Recently, the excited-state structures of the aromatic carbonyl molecules benzaldehyde and acetophenone were studied, and a bifurcation of pathways from the excited state was discovered [22, 23].

To study the structural dynamics of surfaces, interfaces, thin films and crystals, ultrafast electron crystallography (UEC) has been developed in this laboratory. Surfaces and interfaces are very important in chemical reactions and nanotechnology. The two-dimensional nature of surfaces and thin films, as oppose to bulk materials, induces interesting physical properties. We are especially interested in studying large molecules, wherein most of them cannot be made into gas phase. The order and repeat units in crystalline sample of the molecules generate three-dimensional diffraction, which allows for determination of the complicated molecular structures, as in steady-state protein crystallography.

In the last five years, UEC apparatus has been designed and assembled in our laboratory. UEC methodology has been developed and demonstrated with many experiments. Semiconductor surfaces were studied as first experiments [24, 25]. Absorbed small molecules, such as water/ice on semiconductor surfaces [26], and self-assembled monolayers of alkanethiols and thio-derivatized hemes on gold surfaces [27], were also studied. Recently, Langmuir-Blodgett films of complicated molecules — fatty acids [28] and phospholipids [29] — were studied, opening the gate to the study of biomolecules.

In the following chapters, the development of the UEC technique and its applications will be reported. Chapter 2 gives a detailed description of the UEC apparatus and the experimental operations with the apparatus. Chapter 3 explains the methodology of UEC, including the experimental aspects and the principles of analysis. Chapter 4 begins the results section with the early experiments on semiconductor surfaces. Studies on absorbsed fatty acids and phospholipids in the crystalline form of Langmuir-Blodgett films are presented in chapters 5 and 6. The steady-state studies of static structure and thermal behavior are described in chapter 5. The structural dynamics studies following a temperature jump induced by femtosecond laser are depicted in chapter 6, based on the static structure determination and are compared to the equilibrium temperature dependence. Chapter 7 concludes the thesis and the perspective of UEC is discussed.