Chapter 7

Conclusion

The advance of experimental techniques contribute significantly to the research of physics. In the study of ultrafast dynamics, laser spectroscopy has pushed the time resolution to femtosecond and attosecond. By using the femtosecond 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. But when the process under study involves structural change, only indirect structural information can be obtained from ultrafast spectroscopy.

Combining the ultrafast time resolution in picosecond to femtosecond and the atomic spacial resolution in sub-ångström, ultrafast diffraction techniques are developed to study the structural dynamics directly. Comparing to X-rays, electrons have larger scattering amplitude, penetrate less and better match the optical penetration depth in most samples, and 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 diffraction and imaging experiments of laboratory scale.

Using the fs laser pulse as pump pulse and the ultrashort electron pulse as probe pulse, ultrafast electron crystallography (UEC) is developed as a pump-probe experiment, with the ultrafast time resolution in ps and the atomic spacial resolution in pm, to elucidate the structural dynamics in solids, surfaces and macromolecular systems.

The UEC apparatus consists a homemade ultrahigh vacuum (UHV) chamber system and a commercial femtosecond laser system with optical interfaces. The fs laser system provides both the laser pulses for the generation of ultrashort electron pulses and those initiating the reactions to be studied. UHV is required for the surface experiments, and the chamber system includes the scattering chamber, the sample preparation chamber and the load lock chamber. The scattering chamber connects to the electron gun system and the imaging system, where the electron pulses are generated, focused and recorded after they are diffracted by the samples. A mechanical system allows the sample to be transferred between the chambers under UHV, and manipulated for the diffraction experiments. A homemade gas handling system with a microcapillary array beam doser augments the UHV chamber system to deliver gas adsorbates to the surface in a controlled and quantitative way.

The principle of the UEC analysis is from the static electron crystallography, with emphasis on RHEED for surface studies. As a pump-probe experiment, accurate characterization and alignment of the fs laser pump pulse and the ultrashort electron probe pulse were carried out, and the time zero and time resolution were determined. The diffraction patterns at each time step are analyzed to obtain the structural changes, especially the changes in the total intensity of the diffraction peak, the diffraction peak position and the peak width in reciprocal space.

The UEC experiments for surface studies are first demonstrated on semiconductor surfaces, because their surfaces can be relatively easily prepared with different absorbates, and their crystalline and physical properties are well studied. UEC studies on silicon(111) surfaces and GaAs(111) surfaces show coherent nonthermal motions of atoms following ultrafast laser irradiation. The amplitude of atomic motions, the temperature change and the time scales are determined. Experiments on surfaces with molecular absorbates are also carried out, but the challenges of structural disorder and low density prevent more detailed analysis.

Langmuir-Blodgett technique has proven powerful in the preparation of two-dimensional crystalline films. It allows for a controlled layer-by-layer deposition of ordered molecular films, and many different kinds of molecules have been successfully made into LB films. However, the selective preparation of adsorbates with well-defined structures by means of the LB technique is not a trivial task, even for the "simplest" of all LB films, fatty acids and fatty acid salts. The steady-state studies of static structure using UEC without time resolution reveal crystal structures of fatty acid bilayers and multilayers, and their thermal behaviors. The impacts of the substrate, layer thickness and preparation conditions on the film structure are elucidated. We also studied the monolayer and bilayer LB films of phospholipid, which have similar structures to fatty acid but are more complex and are more relevant to biological molecules.

UEC studies of the structural dynamics following a temperature jump induced by femtosecond laser are based on the static structure determination and are compared to the equilibrium temperature dependence. For all LB films (fatty acids and phospholipids) studied, with sub-Å resolution and monolayer sensitivity, it is observed that a coherent anisotropic expansion solely along the aliphatic chains happens at picosecond time scale, followed by nonequilibrium contraction and restructuring at longer times. This motion is indicative of a nonlinear behavior among the anharmonically coupled bonds on the ultrashort time scale and energy redistribution and diffusion on the longer time scale. The effects of different molecules, layer thickness and substrate on the dynamics are examined. Unlike monotonic disordering in the equilibrium heating, a transient structural ordering was revealed on the picosecond time scale. Interestingly, it is found that this transient ordering is more pronounced and lasts longer at higher static sample temperature.

The combined structures (unit cell and orientation) and dynamics (after femtosecond laser heating) on LB films not only provide insights into the nature of atomic motions and energy transfer — coherent versus diffusive — in fatty acids and phospholipids, but also demonstrate the possibility of using UEC and LB films to study complex macromolecules. It will be very interesting to study other molecular dynamics, for example the photo-isomerization of retinal [144].

UEC is a very versatile technique. Although so far most UEC studies were done with reflection electron diffraction, the UEC apparatus was designed also capable of transmission experiments. In transmission mode, the velocity mismatch between the laser and electrons is much smaller, and more Bragg spots can be obtained. The challenge with UEC in transmission mode is that the nondestructive structural change induced by laser inside the crystal, where the transmission electron diffraction probes, might be very small. The preparation of thin samples for the transmission experiments can also be difficult.

UEC is developed to study the structural dynamics of various materials. For bulk materials, many physical phase transitions involve structural changes, such as melting, surface reconstruction and solid-solid phase transitions. Also by observing the atomic motions in solids and on surfaces, we could study other physical processes related to phonons. On the other hand, the surfaces provide a template to study ordered molecules, as we have done for fatty acids and phospholipids.

As a pump-probe experiment, UEC can be used to study any structural dynamics induced by fs laser pulses. Although so far most experiments are done with 800nm or 266nm laser, it is possible to excite the molecules in the crystal or on the surface directly by varying the wavelength. Comparing to the gas phase, the excitation energy needed is smaller, though the heating effect will need to be taken into account.

Better time and space resolution will always be the pursuit for future UEC experiments. It has been shown that by better matching the velocity mismatch between the pump laser and probe electron pulses, the time resolution of UEC is improved in reflection mode [32]. Although our experiments are ultimately limited by the electron pulses we have, the single electron experiments provide entirely new ways of thinking [9]. Additionally, with the aid of dynamical diffraction theory, the transient crystal structures can be further refined from the diffraction patterns.

Together with new developments of UED in gas phase for more complex molecules, and new ultrafast electron microscopy (UEM), UEC proved to be a very important experimental technique to study the ultrafast structural dynamics of materials.