

Ultrafast Electron Microscopy:

Watching Atoms Move and Crystals Melt

Garrett K. Drayna and David J. Flannigan
Mentor: Ahmed H. Zewail

Introduction

Imagine being able to actually watch the atoms move inside a grain of salt, or being able to see how ions are transported across the hydrophobic cell membrane.

In order to do this, you would need a completely new type of methodology. This technique would have to be able to combine the very high spatial resolution necessary to actually see atoms (on the order of one angstrom, where one angstrom = 10^{-10} meter) with the high temporal resolution necessary to see those atoms move (on the order of a femtosecond, where one femtosecond = 10^{-15} second). For decades, researchers have relied on static images provided by electron microscopy and static diffraction patterns provided by X-ray crystallography to infer how a system operates. The major drawback to these otherwise very powerful techniques is that no direct experimental evidence is gathered about the structure of the transition states of the system. That is, these techniques can only provide information about the three spatial dimensions; while information about how the system behaves in the fourth dimension – time – remains a mystery. Therefore, to overcome this fundamental problem, a methodology that can access all four dimensions simultaneously must be realized and demonstrated. The development of such a technology would mark a great day in the advancement of human knowledge. Fortunately, that day has arrived with the advent of Ultrafast Electron Microscopy (UEM).

Ultrafast Electron Microscopy

In the Physical Biology Center for Ultrafast Science and Technology (UST) at Caltech, a revolutionary new method of microscopy has been developed that makes the direct observation of the smallest, fastest, and most complicated processes feasible. This new methodology is called Ultrafast Electron Microscopy because of its ability to access the fourth dimension – time – in addition to the three spatial dimensions. Essentially, UEM combines the well-established sub-nanometer (nanometer = 10^{-9} meter) spatial resolution of a standard transmission electron microscope (TEM) with the femtosecond time resolution of an ultrafast laser system. By providing access to these spatial and temporal domains, the direct visualization of the structural dynamics of matter on the atomic-scale and on the time-scale of molecular bond vibrations is now within reach.

The UEM methodology is based upon the stroboscopic pump-probe technique. The main difference between the well-established spectroscopic pump-probe techniques and UEM is that electrons, rather than photons, are used to probe the excited sample. The use of electrons as probes allows for analysis of the actual atomic-scale structural changes induced by the pump laser pulse, because of the much shorter wavelength of fast electrons relative to optical photons from the de Broglie relation. The laser system used for the first-generation UEM, known as UEM1, consists of a diode-pumped, mode-locked Ti:sapphire oscillator, which generates 120 fs pulses of 776 nm laser light with a repetition rate of 80 MHz and an average power of three watts. The repetition rate can be varied by placing an acousto-optic pulse picker in the optical axis. The beam is split into two arms: one that is frequency-doubled to generate near-ultraviolet light, while the other serves as the pump laser and is directed into the UEM column and focused onto the sample. The pulses in the near-ultraviolet arm travel through a variable time delay line and then to a photocathode, which is also housed in the UEM column. Irradiation of the photocathode with near-ultraviolet laser light generates packets of electrons, which are accelerated to 120 keV and probe the photoexcited sample. A conceptual diagram of the UEM technique is shown in Figure 1.

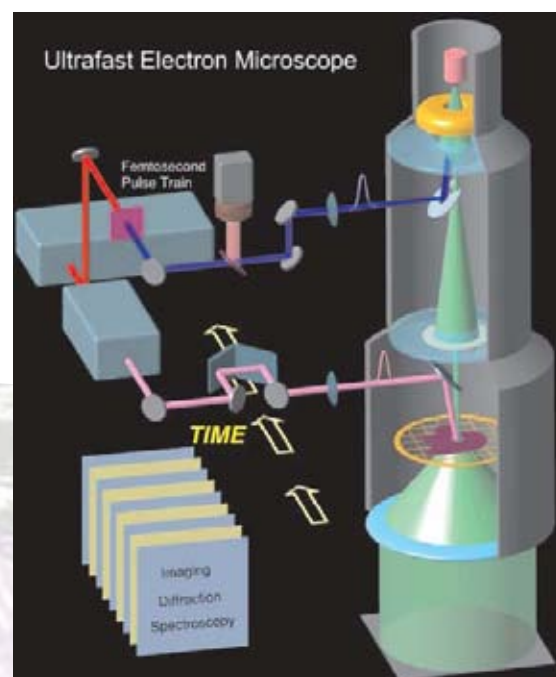


Figure 1. The ultrafast electron microscope. The setup involves interfacing a TEM with a train of femtosecond optical pulses to generate an electron beam in ultrafast packets of as few as one electron per pulse. The other optical beam delivers, after a time delay, initiating pulses at the specimen. Other critical components include the microscope lens system, charge-coupled device camera, and image acquisition and processing software. Figure adapted from Lobastov, V. A. *et al. Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 7069.

As previously mentioned, the UEM is used to resolve structural dynamics via a stroboscopic method because of the very low number of electrons in each probe pulse. Having only a few electrons per packet allows for Coulombic space-charge broadening to be avoided; this broadening would limit temporal resolution due to the increased spread in arrival time of the electrons at the sample. Because each packet contains only a few electrons, an image is not formed after only one pulse due to the

small number of total interactions with the sample. Therefore, to build up a single image the use of several pulses is necessary. Once an image of the sample at a certain time delay is obtained, the time difference between the pump and probe beams is increased and the process is repeated. By changing the time delay between the pump and probe pulses, a series of images can be obtained that are representative of the ultrafast structural dynamics of the material being studied. These images can then be linked together to form a movie of the dynamics under study. In addition to UEM1, which operates at 120 kV, UST at Caltech recently developed the second generation UEM, UEM2, which operates at 200 kV. In addition to electron diffraction and imaging, UEM2 can also operate in a scanning mode (STEM) and is capable of measuring electron energy loss spectra (EELS). The ability of the UEM methodology to reach similar spatial resolutions of a standard TEM is illustrated in Figure 2.

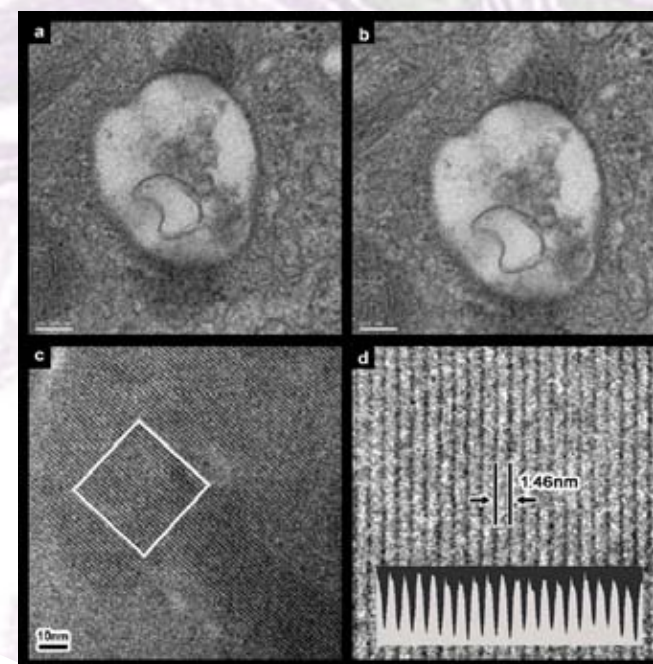


Figure 2. Can you tell the difference?

(a) UEM and (b) corresponding TEM image of a vesicle inside a positively stained rat intestinal cell. The scale bar in the lower left corner of the images represents 100 nm. (c) High-resolution UEM image of a crystal of chlorinated copper phthalocyanine showing the crystal lattice fringes. (d) Magnification of the selected area shown in (c) revealing the 1.46 nm spacing between the copper planes. Panels (a) and (b) adapted from Lobastov, V. A. *et al. Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 7069. Panels (c) and (d) adapted from Park, H. S. *et al. Nano Lett.* **2007**, *7*, 2545.

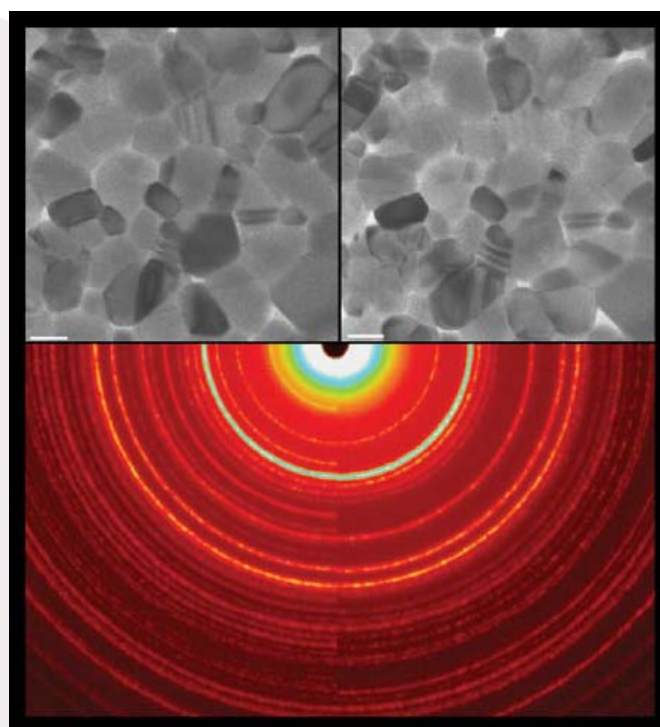


Figure 3. The upper two panels show UEM images of the same region of a polycrystalline VO₂ film obtained before (Left) and after (Right) the laser-induced phase transition. The white scale bar shown in the lower left corner of each figure represents 100 nm. The lower panel shows the composite experimentally observed diffraction patterns from each of the films shown in the upper panels. The diffraction patterns clearly show the change in the ring pattern arising from the change in unit cell symmetry that occurs during the ultrafast phase transition. Figure adapted from Grinolds, M. S. *et al. Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 18427.

Resolving Nanoscale Mechanical Motion with UEM

One of the first studies done using UEM was on the structural dynamics of the insulator-to-metal phase transition in vanadium dioxide (VO₂). From previous work, it was known that VO₂ made this transition on an ultrafast time-scale, making it an ideal candidate for study with the new UEM system. The results were nothing short of spectacular. Not only was a detailed profile of the structural phase transition on the sub-picosecond timescale (picosecond = 10⁻¹² second) elucidated in diffraction mode, corresponding real-space images revealed striking changes in contrast within crystalline VO₂ domains (Figure 3).

More recently, UEM has been used to discover previously unknown photoinduced mechanical motions in an otherwise well-characterized metal-organic molecular material, copper 7,7,8,8-tetracyanoquinodimethane (Cu-TCNQ). This material belongs to a large class of charge-transfer complexes known as quasi one-dimensional molecular semiconductors. Many of these materials have phase transitions known as spin-Peierls transitions, which occur as a result of the separation of spin-paired electrons located on neighboring TCNQ radical anions. The separation of the paired electrons results in an ultrafast movement of stacked TCNQ molecules away from one another but only along one of the three crystallographic axes. This phase transition can be initiated by near-infrared laser light.

To observe these dynamics, single crystals of Cu-TCNQ ranging in size from several micrometers to tens of nanometers were synthesized directly on the surface of an amorphous silicon nitride (Si₃N₄) film that was 50 nm thick. What was observed with UEM was striking and would not have been possible with a conventional TEM. After fracturing a single crystal with laser pulses, it was discovered that the crystals would expand preferentially along one crystallographic axis when exposed to laser light. When the laser light was blocked, the crystal would return to its original structural configuration. By pulsing the laser repeatedly, it was shown that this expansion and contraction

was robust over many cycles (Figure 4). Analysis of the crystal lattice spacing as a function of laser fluence confirmed that the anisotropic expansion observed on the nanoscale originated from atomic-scale motions.

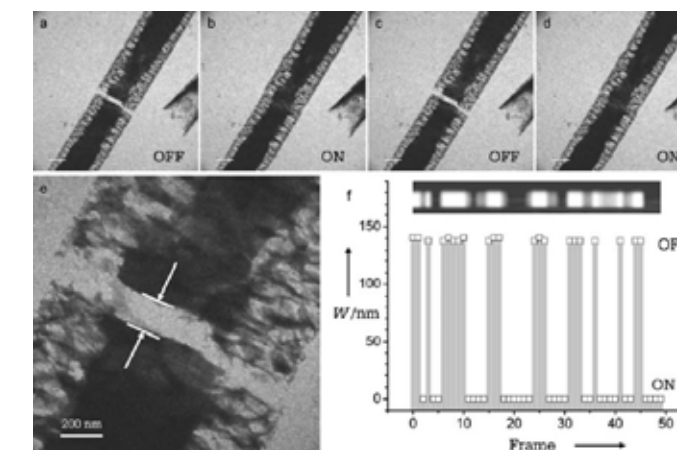


Figure 4. (a – d) UEM images of the expansion and contraction of a Cu-TCNQ single crystal. The sequential views (scale bar = 500 nm) show the fractured single crystal in the “OFF” state (a, c; no pulsed-laser irradiation) and in the “ON” state (b, d; pulsed-laser irradiation). (e) Higher-resolution image of the crystal in the “OFF” state illustrating the section within which quantification of the reproducibility of the expansion/contraction was performed. (f) Plot showing the results of a sequence of “ON” and “OFF” cycles. The channel width (*W*) varied from 0 (pulsed-laser irradiation) to 140 ± 5 nm (no pulsed-laser irradiation) over a series of 50 frames. The bar above the data points illustrates the modulation in a memory recording. Figure adapted from Flannigan, D. J. *et al. Angew. Chem., Int. Ed. Engl.* **2007**, *46*, 9206.

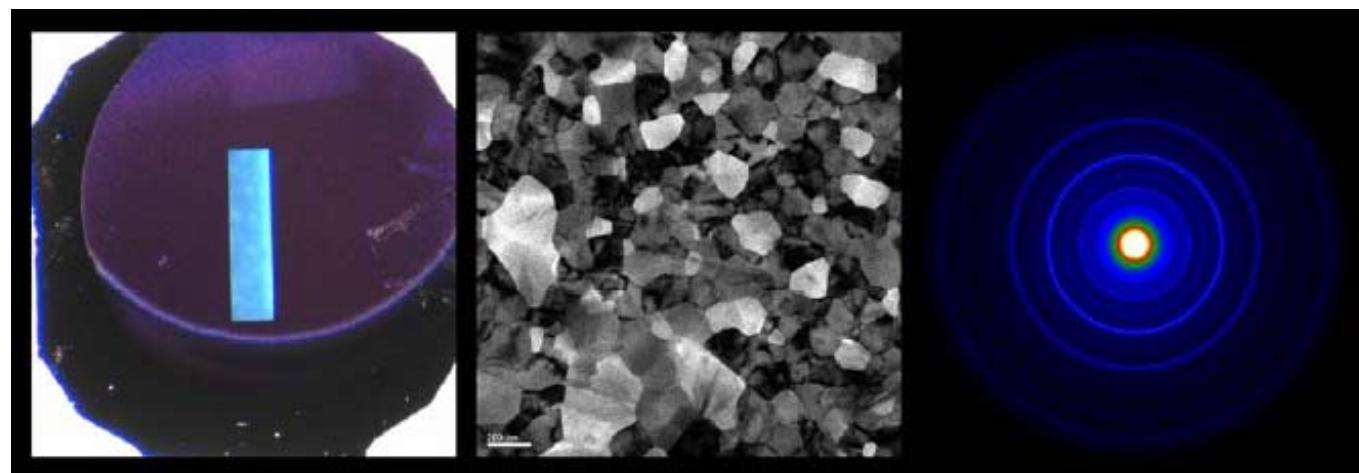


Figure 5. The series of panels show the following: (Far-left) Optical microscope image of a thin K-TCNQ film (blue/purple) deposited onto a Si₃N₄ membrane TEM grid. The light-blue rectangle in the center of the grid is a 2.0 x 0.5 mm window used for specimen viewing in TEM. (Center)

UEM image of the K-TCNQ polycrystalline film shown in the far-left panel. The scale bar in the lower left corner represents 200 nm. (Far-right) Rotationally-averaged UEM diffraction pattern obtained from the K-TCNQ polycrystalline film shown in the center panel.

Looking to the Future

Another TCNQ charge-transfer complex that has been widely studied is potassium TCNQ (K-TCNQ). Previous femtosecond optical reflectivity studies on K-TCNQ single crystals have indicated that the photoinduced melting of the spin-Peierls phase in this material occurs on the sub-picosecond timescale. While reflectivity studies of this sort are effective at providing indirect evidence of structural changes, the direct observation of the ultrafast motion of molecules in the unit cell requires a different technique. The UEM methodology is well-suited for elucidating this motion.

As is true of all electron microscopy techniques, the preparation of high-quality samples for UEM studies is absolutely critical to the success of the experiments. Because of this, a novel sample preparation method was developed to prepare polycrystalline films of K-TCNQ directly on thin (30 nm) Si₃N₄ membranes. After cleaning the surface of the Si₃N₄ membrane with argon plasma, a thin layer (20 nm) of potassium iodide (KI) is deposited onto the membrane via thermal evaporation. The sample is then placed in a custom-machined holder, which also serves as a TCNQ reagent source, and the entire apparatus is heated to 120 °C under a steady flow of dry argon. As the apparatus warms, the TCNQ sublimates and the vapor reacts with the thin KI film to form K-TCNQ (Figure 5). Characterization of

the thin K-TCNQ film with Fourier transform infrared spectroscopy and surface X-ray photoelectron spectroscopy showed that this synthetic methodology produced very pure films of K-TCNQ with no residual iodine. This represents a significant advance in sample quality over previously reported methods for synthesizing thin K-TCNQ films. Now with a robust way to synthesize these films, work is currently focusing on using UEM to directly visualize the photoinduced structural dynamics of this intriguing molecular material.

There is much promise for using UEM to study the structure-dynamics-function relationships present in complex biological systems such as ribosomes and cell membrane channels. Indeed, elucidating how physical forces affect global function of cellular components at the atomic level is a major goal of UST at Caltech. While the TCNQ-based materials currently under investigation are much simpler than most cellular systems, they do represent an increase in complexity over simple metals and metal oxides previously studied, and are held together with the same forces as those present in complex biological structures. Clearly, the knowledge gained by studying these molecular materials with UEM will be invaluable when applying this methodology to more complex biological systems.

Acknowledgments

Garrett Drayna is a second year undergraduate at Caltech. He would like to thank the Gordon and Betty Moore Foundation, the Air Force Office of Scientific Research, and the National Science Foundation all for funding this research, the Caltech Summer Undergraduate Research Fellowship (SURF) Program, and Drs. Vladimir Lobastov and Jonas Weissenrieder for insightful discussion and guidance. He would especially like to thank his mentor, Prof. Ahmed Zewail, and his co-mentor, Dr. David Flannigan, for their inspiration and guidance.

Further Reading

1. Zewail, A. H. 4D Ultrafast Electron Diffraction, Crystallography, and Microscopy. *Annu. Rev. Phys. Chem.* **2006**, *57*, 65-103.
2. Flannigan, D. J.; Lobastov, V. A.; Zewail, A. H. Controlled Nanoscale Mechanical Phenomena Discovered with Ultrafast Electron Microscopy. *Angew. Chem., Int. Ed. Engl.* **2007**, *46*, 9206-9210.
3. Grinolds, M. S.; Lobastov, V. A.; Weissenrieder, J.; Zewail, A. H. Four-Dimensional Ultrafast Electron Microscopy of Phase Transitions. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 18427-18431.
4. Baum, P.; Yang, D.-S.; Zewail, A. H. 4D Visualization of Transitional Structures in Phase Transformations by Electron Diffraction. *Science* **2007**, *318*, 788-792.
5. Gedik, N.; Yang, D.-S.; Logvenov, G.; Bozovic, I.; Zewail, A. H. Nonequilibrium Phase Transitions in Cuprates Observed by Ultrafast Electron Crystallography. *Science* **2007**, *316*, 425-429.