Chapter 3.
UED Experimental Methodology

This chapter describes the physical setup required to perform UED experiments. The account of the apparatus will be followed by descriptions of the methods used to calibrate the experiment as needed in the data analysis. Topics such as time-zero, velocity mismatch, time resolution, camera distance, and pulse widths will be addressed.

3.1 The ultrafast electron diffraction apparatus

The third generation UED apparatus has been presented elsewhere,[1] but herein will be covered in further detail. The UED experiment is a combination of several components that will be addressed separately: a femtosecond laser system, a high-vacuum chamber and molecular beam, a high-voltage ultrafast pulsed electron gun, a CCD detector, and a high-temperature inlet system. Simply summarized, the beam from the femtosecond laser system is split and the more intense pulses are focused and directed

into a molecular beam to initiate reaction. The weaker femtosecond laser pulses are focused onto a back-illuminated silver photocathode in the electron gun to generate electron pulses by the photoelectric effect. The pulses are accelerated and focused to meet the excitation laser and the molecular beam in a mutually perpendicular arrangement. Scattered electrons are detected by a CCD camera at the terminus of a phosphor, fiber-optic, image-intensifier chain. The excitation laser pulses may be delayed to provide time-dependent diffraction patterns. A schematic drawing of the setup is shown in Fig. 3-1.

3.1.1 Femtosecond Laser System

An amplified femtosecond laser system (Spectra Physics) is used in UED experiments (see Fig. 3-2). It consists of a mode-locked Ti:Sapphire oscillator (Tsunami) that delivers seed pulses (6 nJ; 800 nm; 60 fs; 80 MHz) to a dual-stage Ti:Sapphire amplifier (Super Spitfire). The output of the oscillator is spectrally evaluated to determine its center wavelength and bandwidth (10–12 nm at FWHM) before it enters the amplifier. In each stage of the amplifier is a Ti:Sapphire rod pumped by about 10 W of green (either 528 or 532 nm) pulsed at 1kHz. The amplifier (see Fig. 3-3) functions by chirped-pulse amplification where the femtosecond-duration seed pulse is stretched by a grating, amplified, and then compressed back into the femtosecond regime. The first amplification stage is regenerative where the stretched pulse occupies a cavity passing multiple times through the gain medium until maximum amplification is reached and it is released by a Pockell's cell. The second stage of amplification simply entails two passes through the second Ti:Sapphire rod. Pulses leaving the amplifier (2.3 mJ, ~120 fs, 800

nm; 1 kHz; horizontally polarized) are temporally characterized by an auto-correlator (Positive Light) and frequency-tripled in a third-harmonic generator module (Uniwave) to provide the ultraviolet pulses (400 μJ; 266.7 nm) needed for electron generation and reaction pumping.

After the tripler, the pulsed UV beam then enters the "optics table" (see Fig. 3-1) where a beam-splitter separates it into an electron-generation and excitation beam. The electron-generation beam (~7 % of the original beam) passes through two irises closed to ~1 mm to attenuate the beam and improve its transverse mode. The beam also passes through a 10% transmission neutral density filter (NDQ100) for further attenuation. A lens of focal length of 300 mm then focuses the beam into the electron gun. The significant attenuation of the electron-generation beam is necessary to prevent damage to the photocathode, which must maintain its integrity for the duration of the experiment. A computer controlled, modified camera shutter prevents electron extraction except during acquisition.

The excitation beam (93% of the original beam from the tripler) is time delayed by a translation stage before it, too, is focused by a moveable lens into the diffraction chamber. The translation stage has a range of approximately 1.5 ns; a laser pulse can arrive in the scattering chamber ~1 ns before an electron pulse.

3.1.2 Picosecond pulsed electron source

Electron pulses are generated using a back-illuminated picosecond electron gun.[2] The pulsed electron gun is housed in a chamber (Fig. 3-4) separated from the main diffraction chamber by a 2 mm aperture. The chamber is pumped by a BOC Edwards

turbo-molecular pump (EXT 250; ~200 l/s) by which pressure is maintained at ~10^{-7} torr during experiments (nearly independent of molecular beam operation). Before entering the chamber, laser pulses pass through two irises (each at ~1 mm) and a NDQ100 (10 % transmittance) to attenuate the beam such that the photocathode is not damaged over the course of the experiment. Laser pulses are focused with a lens and enter the chamber to impinge on a back-illuminated photocathode. The lens is mounted on a translation stage so adjustment of the spot size can be made and damage due to over-focusing averted. The photocathode consists of a stainless steel mount to which a sapphire window is fastened by silver paste. A silver coating of 25 nm is deposited on the window using a BOC Edwards Auto 306 Vacuum Coater. Electrons are ejected by the impinging ultraviolet light by the photoelectric effect. The kinetic energy of the ejected electrons is described by

$$KE = h\nu - \Phi, \tag{3-1}$$

where Φ is the work function of the material. Silver, used exclusively in UED, has a work function of 4.3 eV (averaged over several literature values).[3,4] Little change in work function is noted between bulk silver and thin film silver surfaces.[4] The work function is further lowered by the effect of the electric field.[5]

$$\Delta\Phi = -e\sqrt{\frac{e \cdot E}{4\pi\varepsilon_0}}, \tag{3-2}$$

where E is the extraction field in V/m, e is the fundamental charge, and ε_0 is the permittivity of a vacuum. A voltage of 30 kV is maintained on the photocathode via high-voltage feedthrough and a high voltage power supply, and a grounded extraction anode is

positioned 3 mm from the coated surface by ridged, insulating Macor ceramic spacers (see Fig. 3-4). The electron beam passes through a 200 μm pinhole on the extraction anode to clean the profile. Accelerated electrons have $\lambda_{\text{de Broglie}} = 0.06979$ Å [Eq. (2-3)] and are traveling at 9.8×10^7 m/s (nearly one-third the speed of light). Leaving the extraction region, electrons are focused with an electromagnetic coil by which the size and shape are optimized (~350 μm FWHM with Gaussian profile, see Section 3.2.2 below). The electromagnetic coil (typically referred to as the magnetic lens) is simply a length of wire outside the vacuum wrapped around the path of the electron beam. A current of ~2 A is passed through the wire, regulation of the current affects the magnetic field experienced by the electron beam and permits its size and shape to be changed. The electrons then pass through the 2 mm pinhole separating the electron gun chamber from the scattering chamber. Once in the scattering chamber, two sets of deflection plates (horizontal and vertical) and a set of streak plates (vertical) are used to manipulate the electron beam's path and its final position on the detector (see Fig. 3-5). The streak plates are used in the streaking experiments that measure the temporal profile of the electron pulses.[6] In addition, they are also needed to move the beam outside of the filtered region on the detector (see below) where the number of electrons present in a single pulse may be measured accurately.

The photocathode must undergo a period of "warming up" where the number of electrons increases over time with exposure of the photocathode to the laser. This typically takes 12 hours, after which the beam is stable and ready to be used in UED experiments.

3.1.3 Diffraction Chamber and Molecular Beam

The scattering chamber (Figs. 3-1 and 3-6) is separated from its primary pumping system (Varian VHS-6 oil diffusion pump, 2400 l/s) by a pneumatic gate valve. The pump permits vacuum to 10^{-8} torr when the molecular beam is not running. Pressures during the experiment can be as high as 3×10^{-4} torr. Data noise caused by electron scattering from background gas is minimized by the use of a liquid nitrogen cryo-trap that is a baffle (Varian) attached to the diffusion pump. After many hours of experimentation with most organic compounds, background gas can lead to the formation of a layer of polymeric coating on the inlet window, which reduces the laser transmission.

Another source of noise, scattered light from the excitation laser pulses, is minimized by a baffle that extends approximately 10 cm from the CaF_2 inlet window. After crossing the molecular and electron beams in the interaction region (all beams mutually perpendicular), excitation laser light exits the chamber through a quartz window at Brewster's angle.

Several versions of the sample inlet manifold have been used in UED. It originally began with a glass bulb connected via ultratorr fitting and a silicone o-ring where the sample was heated and conveyed into the needle. The system was modified, however, to permit higher boiling point molecules. The glass bulb was replaced with a stainless steel reservoir (about 300 mL capacity) clamped with a custom band heater (Watlow). The remainder of the manifold is constructed of stainless steel. The reservoir and the valves can tolerate heats of up to 400 ºC. A second manifold is connected to the high-temperature portion of through a fine-metering needle valve. This manifold allows

CO_2, Xe, and butadiene access to the nozzle. The manifold is also connected to a mechanical pump for evacuation during sample changes.

The nozzle tip, with a 180 μm aperture, is connected to the manifold via a stem running through an insulated flange. The nozzle (and stem) is heated by a tight wrap of insulated high-resistance thermocouple wire and the manifold is wrapped in fiberglass heating tape. The heating systems of each unit are monitored and controlled separately. The temperatures are optimized to prevent condensation clogging and thermal decomposition while still delivering an appropriate amount of sample to the interaction region. Vaporized sample from the reservoir passes through the manifold, stem, and nozzle to form a molecular beam at the nozzle temperature via effusive expansion.

3.1.4 Detector and Data Acquisition

Detection of the electron diffraction signal is done with a CCD (charge-coupled device) camera at the end of an image-intensifier fiber-optic chain (see Fig. 3-7). The phosphor scintillator is comprised of a fiber-optic disc (diameter = 8 cm) with a coating of P-47 phosphor. A 300 nm layer of aluminum is coated over the phosphor to absorb any scattered UV light. The phosphor causes impingent electrons to be converted to photons which may then travel through the fiber-optics. (For some data on the conversion efficiency of P-47 phosphor, see Fig. 3-8.) A radial symmetric neutral-density filter is coated on the reverse side of the fiber-optic disc in order to increase the dynamic range of detection (as seen in Chapter 2, the electron diffraction signal decreases rapidly with scattering angle). The filter extends 15 mm from the center of the plate (the fiber-optic face plate has a diameter of 80 mm). The center portion of the filter has a transmission of

1% that increases to 100% at the edge (see Fig. 3-9). Photons produced by the phosphor and that pass through the fiber-optic disk and the filter then travel through a fiber-optic reducing taper to the image intensifier (Hamamatsu), which amplifies the signal via a microchannel plate. Simply, channels are coated with a photocathode material that converts the photons to electrons that then are multiplied by their collisions in the channels. These electrons encounter another layer of phosphor that converts the electrons to an amplified signal of light. A voltage across the plate determines the signal gain appreciated. The output photons traverse a second fiber-optic reducing taper and are detected by a CCD camera (Photometrics, KAF-1000). The CCD camera is cooled by a liquid circulator-backed thermoelectric chiller to –40 ºC in order to reduce noise. The entire setup is capable of single electron detection (Section 3.2.1). The CCD camera consists of a 1024×1024 pixel array. The effective pixel size is 57.8 μm on the side of the phosphor screen, and pixels are binned 2×2 during experiments.

Since the vast majority (~99 %) of the electron beam passes through the molecular beam without being scattered, a small metal Faraday cup mounted on an aluminum strip covers the center of the phosphor scintillator to prevent saturation of the detector. In addition, the image-intensifier itself has a null stripe bisecting along the vertical, separating the left and right halves, which can be operated separately. Exposure of the CCD for data acquisition is entirely computer controlled. Standard exposure time is 240,000 pulses (4 minutes). Data acquired for xenon (Air Liquide, 99.995 %) is used to determine the filter's effect on the data. Multiple exposures (typically 100) are acquired

and averaged in the data processing. Conversion of the pattern data to the scattering intensity curves used in the data analysis will be dealt with in detail in Chapter 4.

3.2 Calibrations

3.2.1 Number of electrons per pulse

In order to determine the number of electrons contained in each pulse, the response of the detector to a single electron must be determined. The electron beam is attenuated and defocused using the magnetic lens to such an extent that individual electrons are spread out and can be seen independently. The arbitrary digital intensity units (ADU) given by the CCD for each electron are then recorded and the data is fit with a log-normal distribution of the form

$$y(x) = y_0 + A \cdot e^{\frac{-[\ln(x/\mu)]^2}{2\cdot\sigma^2}}, \tag{3-3}$$

where y_0 is the baseline, A is the scaling factor, μ is the mean of the distribution, and σ is the standard deviation. μ provides the needed value, which was determined to be 46.85 ADU/single electron/pixel at 875 V image intensifier gain (see Fig. 3-10). The focused beam can then be directed outside of the filtered region and its entire intensity recorded on the detector to determine the total number of electrons in the pulse. The amount of laser light allowed into the electron gun is regulated in order to optimize the number of electrons – which is typically 3×10^4/pulse. Shot-to-shot stability of the electron pulses, also critical, is tested by measuring the intensity over 100 electron shots (see Fig. 3-10). Problems in the stability of the electron gun are usually caused by problems with the

photocathode itself. Arcing within the electron gun is one of the major problems that must be avoided in order for an experiment to succeed. An electron gun that cannot hold the voltage must be removed, parts cleaned or replaced, and rebuilt.

3.2.2 Electron pulse spatial size

When the electron beam is moved outside of the filter region the spatial horizontal and vertical profiles of the beam can be accurately determined. The two-dimensional intensity profiles of 100 electron shots are averaged. The horizontal and vertical profiles of the averaged electron pulse are then each fit with a Lorentzian distribution of the form

$$y(x) = \frac{A}{1 + 4\left(\frac{x - x_0}{w}\right)^2} - c, \tag{3-4}$$

where A is a scale factor, c is the intensity baseline, x_0 is the x position of the maximum of the distribution and w is the FWHM (see Fig. 3-11). The magnetic lens current is adjusted in order to make the beam circular and to optimize its size. The typical size is $w_{vertical} \approx w_{horizontal} \approx 350\mu m$.

3.2.3 Electron pulse temporal width

The temporal width of electron pulses is approximately the sum of three major broadening contributions. First is the initial velocity spread of the electrons due to the distribution of photon energies in the pulse incident on the photocathode. Second is the effect of that distribution as the electrons travel from the source. Slower electrons will lag behind faster ones and become farther apart as the path length increases. Third is space-charge broadening, which is a feature of the close packing of repulsive negative charges

within the ultrafast electron pulse. Space-charge broadening causes electrons in the front of the pulse to be accelerated forward (and away from the remainder of the beam) while electrons in the rear are decelerated and pushed backward from the beam. Using the equations[7] for the initial temporal spread

$$\Delta t_{init} = \frac{\sqrt{2m_e \Delta\varepsilon}}{e \cdot E}, \tag{3-5}$$

where $\Delta\varepsilon$ is the energy spread of the electron-ejection pulse and E is the extraction field strength. And, for the broadening in travel

$$\Delta t_t \approx L\sqrt{m_e / 8}\,\frac{\Delta\varepsilon}{(e \cdot V)^{3/2}}, \tag{3-6}$$

where V is the acceleration voltage. For UED, $\Delta t_{init} \approx 9\,fs$ and $\Delta t_t \approx 120\,fs$. Having measured the final electron pulse widths (see below), the largest component (by far) of the overall temporal width of the electron pulses can be assigned to space-charge effects. Possible modifications to the apparatus to minimize broadening effects would include increasing the extraction field and shortening the overall electron path length.

The total temporal width of electron pulses in UED is measured by performing streaking experiments. Such experiments are conducted using a photo-switch that activates an electric field between the streak plates as an electron pulse passes through. The process spreads the pulse and the resulting spatial pattern on the detector can be related to the temporal profile. These experiments were conducted for many electron pulses each with a different spatial size and number of electrons contained within. Hence, electron density calculated using the number of electrons, N_e, $w_{vertical}$, and $w_{horizontal}$,

which are measured prior to every experiment, can be related to the temporal width such that streaking experiments do not have to be performed often. The relationship between the current density, ρ_e, and pulse width, τ_e, takes the form of an allometric law (see Fig. 3-12).

$$\tau_e = a + b \cdot \rho_e^{\,c} \tag{3-7}$$

Interestingly, the intercept, *a*, fit to the streaking data predicts a limit of 0.9 ps when N_e approaches zero. The parameters *a*, *b*, and *c* have fit values of 0.88 ± 0.47, $8.4 \times 10^{-6} \pm 5.9 \times 10^{-6}$, and 1.0 ± 0.047, respectively. An electron beam of 30,000 electrons/pulse with $w_{vertical} = w_{horizontal} = 350\mu m$ has an approximate temporal pulsewidth of 4.3 ps. Comparing this value to the temporal spreads given by Eqs. (3-5) and (3-6) it is clear how important the space-charge effects are to the overall τ_e. It should be noted, however, that in the time since the streaking calibrations were performed the electron gun has been modified (higher extraction field, 10 kV/mm, achieved by implementing shorter Macor spacers); the pulsewidths calculated using Eq. (3-7) with the above fitted parameters likely represent the upperbound of τ_e.

3.2.4 Molecular beam size

The excitation laser beam size (estimated by the focal length of the focusing lens and the distance to the interaction region), the electron beam size (measured directly on the detector), and the molecular beam size (described herein) are adjusted to make them of similar value. The intention is to maximize the number of excited molecules that will be scattering the electron pulse thereby providing the best diffraction signal from the

transient species as possible. The molecular beam for size calibration is formed via an effusive expansion of CO_2 (Air Liquide, 99.5%) The size of the molecular beam is calculated by measuring the total intensity of scattered electrons (proportional to the number of scattered electrons) as the molecular beam is moved across the electron beam. The scattering intensity at all nozzle positions is fit with the Lorentzian distribution defined in Eq. (3-4), as shown in Fig. 3-13. Following theory of Lorentzian profiles, the electron beam width is deconvoluted from the measured width by subtraction to produce the FWHM of the molecular beam, w_m.

$$w_m = w - w_e \tag{3-8}$$

Like for the laser beam and electron beam, the desired w_m at the interaction region is approximately 350 μm. Typically, the nozzle must be 800–900 μm above the center of the electron beam to attain this proper size.

The molecules in the interaction region of a UED experiment are effectively isolated and collisionless. The actual collisional frequency, *z*, may be derived using the Maxwell distribution of speeds

$$f(v) = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} v^2 e^{-\frac{\mu v^2}{2RT}}, \tag{3-9}$$

where *v* is the particle velocity and M is the molar mass.

$$z = \frac{\sigma \cdot \bar{c}_{rel} \cdot p}{kT}, \tag{3-10}$$

where p is the gas pressure, σ is the cross-section approximated by πd^2 (d is the radius of the particle), and $\bar{c}_{rel}$ is the average relative velocity derived from Eq. (3-9) as $4\left(\frac{RT}{\pi M}\right)^{1/2}$. Assuming a molecule is spherical with a diameter of 7 Å and a mass of 100 amu, and the molecular beam has a pressure of 0.53 torr (see Appendix I) and a temperature of 500 K, the collisional frequency is calculated as 2.29×10^5 s^{-1}molecule^{-1} or about 1×10^8 total collisions per nanosecond for the interaction region containing 4.39×10^{11} molecules. This amounts to <1% of molecules undergoing a collision on the time scale of UED experiments.

3.2.5 Experimental time-zero

Optimizing the overlap between the electron, laser, and molecular beams in the scattering chamber and determining the temporal relationship between electron and laser pulses are done simultaneously. The three beams interact in a mutually perpendicular arrangement with the molecular beam arriving from the top. Rough overlap optimization of the molecular beam with electron beam and laser beam is aided by the shadow cast by the nozzle and viewed on the CCD and through the outlet window, respectively (see Fig. 3-14). Overlap is fine-tuned by observing and maximizing a photoion-induced lensing effect on the electron beam.[8] Gas (1,3-butadiene, Aldrich, >99%) is delivered to the scattering chamber via the inlet nozzle and the laser and electron beams are admitted to intersect with it. 1,3-butadiene is used due to its large absorption cross-section at 266.7 nm ($\log(\varepsilon) \approx 4$). The undiffracted electron beam profile is monitored while the time delay of the laser pulses relative to the electron pulses is changed. The focused laser

causes ionization of the gas and the subsequent charge separation alters the shape of the transmitted electron beam. The time at which the electron beam shape begins to change from circular to elliptical gives the *in situ* time-zero.[8] The position of the laser is fine-tuned using the inlet mirror and focusing lens to maximize the lensing effect. The vertical FWHM of the spatial profile of the electron pulses at each time delay is plotted and time-zero is determined (see Fig. 3-14). The ellipticity of the beam (vertical FWHM/horizontal FWHM) is also measured to support the time-zero determination. This procedure functions to within about 10 ps of exact time-zero, which is determined during data analysis (see Section 4.6). It should be noted that since the center of the detector is blocked (see Section 3.1.4) lensing is optimized iteratively on the left and right sides before the time-zero measurements are performed.

3.2.6 Velocity mismatch and overall time resolution

The overall experimental time resolution is governed by the laser pulse width, the electron pulse width (see Section 3.2.3), and the group velocity mismatch. The details of the calculations needed to compute the time resolution have been reported elsewhere,[9] but will be briefly reviewed herein as it applies to these UED experiments. Broadening of overall time resolution in UED experiments is mostly a consequence of velocity mismatch, the slower velocity of the electrons relative to the speed of the excitation laser photons [see Eq. (2-4) for the relativistic electron velocity, v_e]. The slower electron velocity means that the probe electrons and pump laser overlap at different times within the molecular beam; molecules in different parts of the beam will scatter at different time

delays. Assuming the temporal profiles of both laser and electron beams are Gaussian, the temporal broadening due to this velocity mismatch is given by

$$\tau_{vm} = \frac{1}{v_e}\left(\frac{w_l^{\,2} w_m^{\,2}(k\cos\theta - 1)^2 + w_e^{\,2} w_m^{\,2}(k - \cos\theta)^2 + w_l^{\,2} w_e^{\,2}(k^2 - 2k\cos\theta + 1)}{w_m^{\,2}\sin^2\theta + w_l^{\,2} + w_e^{\,2} + w_l^{\,2} w_e^{\,2} / w_m^{\,2}} \right)^{1/2}, \quad (3\text{-}11)$$

where k is the ratio of velocities of the electrons to the laser, v_e/c, and θ is the angle between the electron and laser beams. It is noticeable that τ_{vm} has no dependence on τ_e. In UED, the beams are mutually perpendicular ($\theta = \pi/2$), and Eq. (3-7) reduces to

$$\tau_{vm} = \frac{1}{v_e}\left(\frac{w_l^{\,2} w_m^{\,2} + w_e^{\,2} w_m^{\,2} k^2 + w_l^{\,2} w_e^{\,2}(k^2 + 1)}{w_m^{\,2} + w_l^{\,2} + w_e^{\,2} + w_l^{\,2} w_e^{\,2} / w_m^{\,2}} \right)^{1/2}. \quad (3\text{-}12)$$

It can be seen in Fig. 3-15 that the two major factors determining τ_{vm} are the velocity of the electron pulses and the path length through which the pump and probe beams interact (w_m). In the limit of small beam size or electrons traveling at the speed of light (laser and electron co-propagating), velocity mismatch is eliminated. In the Gaussian beam assumption, the total temporal resolution of the experiment is

$$\tau = \sqrt{\tau_l^{\,2} + \tau_e^{\,2} + \tau_{vm}^{\,2}}, \quad (3\text{-}13)$$

which should make clear that even if the pulsewidth of the electron beam can be reduced into the sub-picosecond time regime, the overall temporal resolution will be limited by the velocity mismatch (see Fig. 3-15). Proposals touting femtosecond time resolution in UED should be mindful of these factors.

3.2.7 Camera length

Although the data refinement procedure will be detailed in the following chapter, here will be a mention of the determination of the camera length, L (see Eq. 2-2). The camera length is determined independently for each experiment since the position of the nozzle (and hence the interaction region) varies slightly. Optimization of lensing (beam alignment) and even cleaning of the nozzle between experiments contribute to this change. The diffraction of carbon dioxide is measured and, using non-linear fitting, the camera length is refined such that the data are consistent with the well known carbon dioxide parameters as reported in the literature.[10] Camera lengths are typically about 13.5 cm.

3.3 References

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