Towards time-resolved electron diffraction

Contact *derek.wann@york.ac.uk*

M. S. Robinson, P. D. Lane and D. A. Wann

Department of Chemistry, University of York, Heslington, York, YO10 5DD, UK

Introduction

Electron diffraction has been a staple method in determining the structures of countless gas-phase and solid-state samples for almost a century.[1] Until recently, most electron diffraction experiments made use of continuous electron beams, where diffraction data for a sample were collected over the course of seconds, minutes or even hours. However, data that are collected over such periods using a continuous beam are time-averaged, causing the structure that is determined to be "blurred" like a photograph of a fast moving object taken with a long exposure.

With the availability of ultrafast lasers, electron diffraction is now tending towards the use of pulsed electron beams that are able to record structural information on the sub-picosecond timescale. The end goal is to take these individual ultrafast images and put them together like the frames on a film reel, creating "molecular movies" that allow us to observe the dynamics of a molecule in real time. Time-resolved electron diffraction (TRED) techniques provide a unique opportunity to be able observe photoinduced changes in molecular structure *directly*, whereas until now we have only been able to *infer* the changes that occur in a species through spectroscopic techniques.

Since the introduction of femtochemical techniques set out by the Nobel Prize winning work of Zewail[2] there has been a drive to introduce ultrafast methods into diffraction techniques. By ionizing a suitable photocathode with an ultrafast laser, it is possible to create pulses of electrons that can interact with a sample on the femtosecond timescale. Combined with pump-probe methods, one is able to investigate the changes that molecules undergo after interaction with external stimuli.[3]

Despite ultrafast X-ray diffraction already being used for observing the dynamics of molecules,[4] electron diffraction (ED) has several advantages: ED is less damaging to samples; electrons have larger scattering cross sections; and electrons are easier to control than X-rays with use of simple electromagnetic instruments. There is also the added advantage that TRED experiments can be carried out relatively cheaply in a tabletop form, unlike with ultrafast X-ray diffraction which generally requires the need for a synchrotron source.

This is a rapidly evolving field that has seen numerous advances in the last five years, including the introduction of RF cavities[5] to compress pulses, and using MeV sources[6] to observe events on shorter time-scales and in a single shot so as to not be restricted to studying reversible systems. Advances have also been made in using stretched electron pulses and streak camera technology[7] in an attempt to observe how molecules change over a single continuous event. However, few have tackled the problem of gas-phase dynamics as it adds an extra layer of complexity. Nonetheless, gas-phase studies give the opportunity to compare results from isolated molecule computational methods, furthering our understanding the subtleties in both fields.

Apparatus

The newly developed time-resolved electron diffractometer, shown in Figure 1, consists of two main chambers: the electron gun chamber, and the diffraction chamber. As the name suggests the first chamber houses the electron gun, which creates pulses of electrons by the ionization of a thin-film gold photocathode using the third harmonic of a Ti:Sapphire laser. These pulses are then accelerated by an electric field between an electrode and anode, which is provided by a potential of up to a 100 kV from a high-voltage power supply connected to the electrode. The electrons pass through an aperture in the anode and into the diffraction chamber.

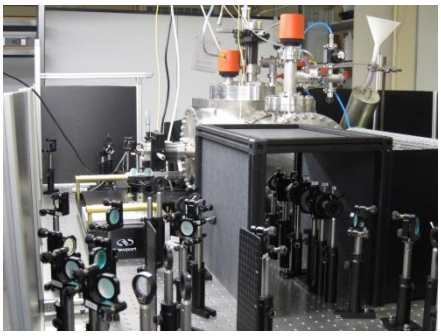

Figure 1: The Wann group 100 kV time-resolved electron diffraction apparatus, with the optics used to generate the 267 nm light needed to create electron pulses.

Once in the diffraction chamber the electrons pass through a magnetic lens, which can alter the transverse spatial properties of the pulse by focusing it to different points along the path of the beam's propagation. Shortly after the lens, the electron beam interacts with a sample of interest, which itself may have been pumped into an excited state (from the same laser source that created the electrons) to induce a change in its structure shortly before the electrons arrive. After scattering from the sample the electrons travel towards the detector, which comprises a microchannel plate (MCP) and phosphor screen. Images produced on the phosphor screen by the scattered electrons are recorded with a charge coupled device (CCD) camera. In front of the detector is a beam cup, which is used to measure the current of the electron beam *via* a picoammeter, whilst also preventing the unscattered electron beam from reaching and saturating the detector.

As the end of goal of this machine is to carry out studies of gas-phase samples, the two chambers are differentially pumped to reduce the likelihood of gas leaking into the electron gun from the diffraction chamber. This helps to prevent the amount of discharging that occurs in the gun, due to the increase in pressure, and allows for experiments to be carried out at higher acceleration voltages for the electrons.

Results

During the 22-week UFL2 loan we were able to calibrate a large number of properties of the new diffractometer, and have taken the first steps towards obtaining time-resolved gas-phase electron diffraction data. First, we determined how the number of electrons per pulse varied with the laser power used to ionize the photocathode. Figure 2 shows how both of these values vary with the optical axis angle of the BBO crystal used to generate

the second harmonic, in the process of generating the third harmonic.

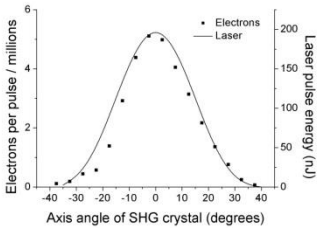

Figure 2: The number of electrons per pulse that are created and pass through an aperture in the electron gun, and how this compares to the pulse energy of the laser used to ionize the photocathode as a function of BBO crystal rotation.

Next we determined the transverse size of the electron pulse. This was achieved for a pulse containing approximately 10,000 45 keV electrons per pulse, with the use of a 500 μm aperture that would only allow a small part of the beam to reach the beam cup. By scanning this aperture over the electron beam it was possible to find the edges and approximate center of the beam, and hence determine the beam size. Figure 3a shows the number of electrons passing through the aperture as a function of distance in two directions (*x* and *y*) perpendicular to the direction of travel of the electron beam. The average FWHM of the pulse was determined to be 435 μm, which is pleasing as it will allow excellent spatial resolution.

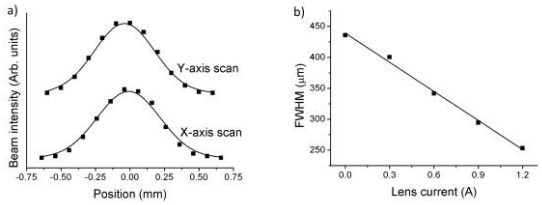

Figure 3: a) Variation in normalized current of the electron beam passing through a 500 μm aperture as a function of position in the x and y directions, and b) variation in FWHM with the current applied to the magnetic lens.

We then spent some time calibrating the properties of a magnetic lens that we have recently built. Figure 3b shows how the FWHM of the electron beam (under the same conditions as in Figure 3a) varies with the current applied to the lens. As one can see, the width of the pulse decreases in a linear fashion as current of the lens increases.

With the properties of the beam calibrated, work moved to obtaining the first diffraction pattern using this apparatus. A 20 nm thick polycrystalline sample of platinum was chosen over a gas-phase sample for its ease of implementation and well-defined diffraction pattern that would allow us to calibrate the machine further and determine its resolution. Figure 4 shows the diffraction pattern obtained from the Pt sample, with the magnetic lens focusing the beam onto the detector.

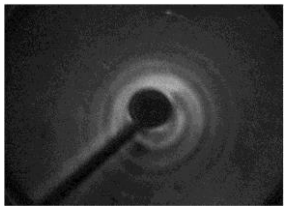

Figure 4: Diffraction pattern obtained from a 20 nm thick polycrystalline Pt sample.

The electron beam itself contained 10,000 electrons per pulse with a repetition rate of 1 kHz. The image is created by stacking 13 images, each with a 28 s exposure time. A background has also been removed from the image which involved collecting data under the same conditions, for the same number of images but without the sample in the path of the electron beam.

To prepare the setup for pump-probe experiments, a simple experiment was then performed to determine the time-zero position for the intersecting pulsed laser and electron beams. This involved passing the electron beam through a fine mesh to produce the grid image seen in Figure 5a. A laser was then introduced perpendicularly to the electron beam, focused on the wire mesh to create a short lived plasma. When the laser and electron beams both arrive at the mesh at the same time ($t = 0$), the electron beam interacts with the plasma, causing the image produced at the detector to become distorted as seen in Figure 5b.

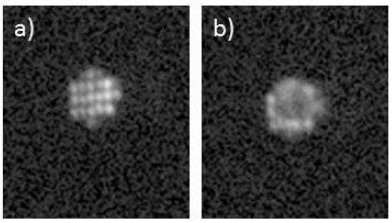

Figure 5: a) Image produced on the detector when electrons pass through a fine mesh, and b) the image produced when a laser-induced plasma is present at the mesh at the same time as the electrons.

Present work and future outlook

During the last week of the project simple gas-phase experiments were performed with argon and carbon tetrachloride (CCl_4) samples introduced *via* an effusive nozzle. Whilst atomic scattering patterns were observed when Ar was injected into the diffraction chamber, only a small amount of molecular scattering was observed for CCl_4.

Since UFL2 has left York a more sophisticated gas delivery system that injects individual pulses of gas when the electron beam arrives at the sample position, has been designed and is currently being built. This addition will allow us to obtain the desired gas-phase diffraction patterns with the apparatus, and allow us to carry out time-resolved gas-phase studies in the near future.

Acknowledgements

We thank the EPSRC for funding (EP/I004122), and Chris Mortimer and his workshop staff in York for help in developing the diffraction apparatus.

References

1. C. Davisson and L. H. Germer, *Nature*, 1927, **119**, 558.
2. T. S. Rose, M. J. Rosker and A. H. Zewail, *J. Chem. Phys.*, 1988, **88**, 6672.
3. M. Gao, C. Lu, H. Jean-Ruel, L. C. Liu, A. Marx, K. Onda, S. Koshihara, Y. Nakano, X. Shao, T. Hiramatsu, G. Saito, H. Yamochi, R. R. Cooney, G. Moriena, G. Sciaini and R. J. D. Miller, *Nature*, 2013, **496**, 343.
4. T. Reusch, D. Mai, M. Osterhoff, D. Khakhulin, M. Wulff and T. Salditt, *Phys. Rev. Lett.*, 2013, **111**, 268101.
5. R. P. Chatelain, V. R. Morrison, C. Godbout and B. J. Siwick, *Appl. Phys. Lett.*, 2012, **101**, 081901.
6. J. B. Hastings F. M. Rudakov, D. H. Dowell, J. F. Schmerge, J. D. Cardoza, J. M. Castro, S. M. Gierman, H. Loos and P. M. Weber, *Appl. Phys. Lett.*, 2006, **89**, 184109.
7. G. H. Kassier, K. Haupt, N. Erasmus, E. G. Rohwer, H. M. von Bergmann, H. Schwoerer, S. M. M. Coelho and F. D. Auret, *Rev. Sci. Instrum.*, 2010, **81**, 105103.