Recent developments towards time-resolved electron diffraction at York

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Introduction

The ability to observe directly the dynamics of molecules is extremely desirable in our attempts to better understand structure-function relationships. In order to achieve experimental dynamics, a direct method of probing molecules with sub-picosecond time resolution is needed. Work performed by Ahmed Zewail and others has already demonstrated the use of diffraction to probe the ultrafast dynamics of molecules,[1] with many early experiments relying on X-rays generated by synchrotron sources in order to produce the required beam brightness and time resolution.[2,3] This reliance on expensive X-rays sources can be overcome by the use of a more manageable diffraction probe: electrons. Electrons have a larger scattering cross section, are less damaging to molecular samples, and are more easily controlled than X-rays. And thanks to the recent developments in ultrafast pulsed lasers, as well as the commercial availability of femtosecond laser sources, electrons can now be produced using "table-top" apparatus. Therefore, time-resolved electron diffraction (TRED) experiments have become a relatively cheap alternative to the use of synchrotron facilities, empowering university-based research groups to study the dynamics of molecules with atomic resolution.

Apparatus

The new time-resolved electron diffraction apparatus (TRED) at York[4] consists of two differentially pumped chambers: a compact electron gun and a versatile diffraction chamber capable of studying both solid and gaseous samples, using time-average or time-resolved electron diffraction experiments.

The compact design of the electron gun overcomes some of the issue of Coulombic repulsion inherent to pulsed electron beams, by minimising the distance between the source of electrons and the sample, significantly improving the time resolution of the apparatus. In the gun chamber electrons are produced by the ionisation of a gold photocathode *via* the third harmonic of a 150 fs, 800 nm, 1 kHz Ti:Sapphire femtosecond laser. Electron bunches containing 10^4 electrons are accelerated across a potential of up to 100 kV and focused using a solenoid lens, reaching the sample with ~357 fs pulse duration.[5] The use of a magnetic lens allows for extensive tunability of the transverse spatial properties of the electron beam, thus improving the spatial resolution of the TRED apparatus. A photograph of the current TRED set-up is shown in Figure 1.

During TRED experiments a pump laser (branched from the same laser source used to produce electrons) is used to excite a given sample, inducing structural changes, shortly before the arrival of the probe electron pulse. As the pulsed electron beam passes through a sample, electrons are scattered towards a detector. The detector assembly comprises a microchannel plate (MCP), a P22 phosphor screen, and a charged coupled device (CCD) camera. In order to avoid detector saturation or damage, a beam cup is placed in front of the detector, blocking the unscattered electrons. Additionally the beam cup is connected to a picoammeter, which allows the current of the electron beam to be measured.

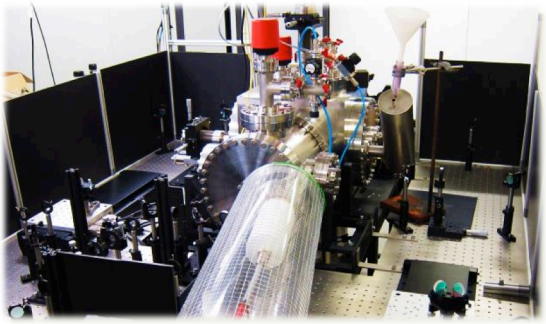

Figure 1: The 100 kV TRED apparatus at York.

A gas-handling system has been coupled to a General Valve pulsed nozzle controlled by a pulse generator, allowing small amounts of gas to be pulsed at 50 Hz into the diffraction chamber in a controlled and reproducible fashion. The temporal overlap between the molecular beam and the probe electron beam is ensured by using the laser signal delay generator (SDG) to trigger the nozzle pulse drive.

Results

The following results were acquired during the UFL2 loan period.

Detector and extraction code improvements

A 20-nm-thick polycrystalline platinum sample was used to calibrate the apparatus and optimise several experimental parameters of the current detector assembly. The MCP arrangement, voltages applied to various components, and the camera settings were optimised to take most advantage of the dynamic range of the CCD sensor, whilst keeping the read-out noise to a minimum. The result of such experimental improvements is shown in Figure 2a). Features that were undetectable six months ago can now be clearly resolved – for example, the double inner ring in polycrystalline Pt diffraction pattern. In addition, the overall noise of the diffraction pattern has been reduced.

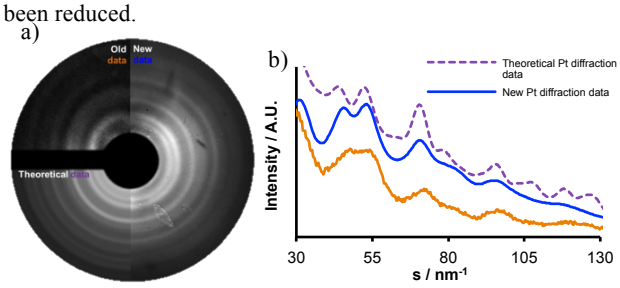

Figure 2: Comparison between theoretical, new and old experimental a) diffraction patterns, and b) diffraction data, collected from a 20-nm-thick polycrystalline platinum sample.

Significant effort has been put into the development of new diffraction data extraction code capable of using beam calibration data to extract high-resolution refinable noise-free molecular intensity curves from diffraction patterns, as shown in Figure 2b).

Visualisation of time-zero

The concept of time-resolved experiments is dependent on the ability to determine accurately the position at which the pump (femtosecond laser) and probe (electron beam) pass through a given sample in both space and time. The determination of time-zero (t_0) was performed using a method first described by Miller *et al*., in which a short-lived plasma, produced by focusing the pump laser at a copper mesh, is used to induce a distortion in the shape of the electron beam.[6] By varying the delay between the pump and probe arrival times, different stages of plasma formation can be probed. This experiment was successfully performed, yielding a series of well-resolved frames with a 670 fs temporal resolution, shown in Figure 3.

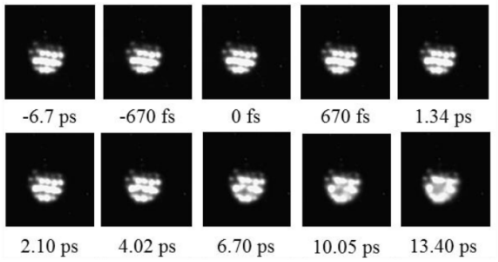

Figure 3: Series of frames showing the interaction between the electron beam and plasma produced by the excitation of a copper mesh with a pump laser at various time delays.

Calibration of the new magnetic lens

A new magnetic lens has been installed and calibrated. This copper-encased 1000-turn solenoid is capable of dissipating heat more efficiently than the old system. The use of this system allows longer data acquisition periods and consequently better signal-to-noise ratios. The maximum focus was found at 1.4 A, a current at which the beam showed a full-width at half-maximum (FWHM) value of 420 µm.

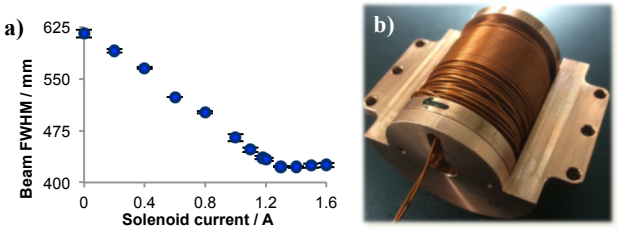

Figure 4: a) Plot of the FWHM of the electron beam *vs*. solenoid current for a 10^4 electrons per pulse electron beam. b) Photograph of the new magnetic lens.

The electron beam was extensively profiled in both its unfocused and fully-focused forms, shown in Figure 5.

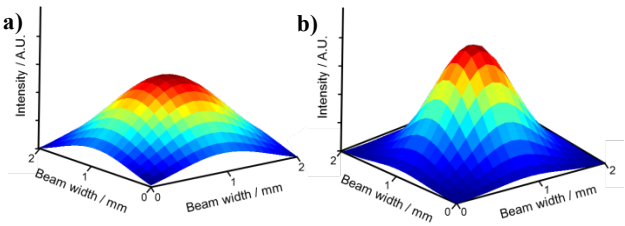

Figure 5: Surface plot of a) an unfocused electron beam, and b) an electron beam containing 10^4 electron focused using a 1.4 A current.

First evidence of gas electron diffraction

During the last weeks of the UFL2 loan the first time-averaged gas electron diffraction patterns were collected using the TRED apparatus at York. Gas electron diffraction data collected for neat CF_4 are shown in Figure 6.

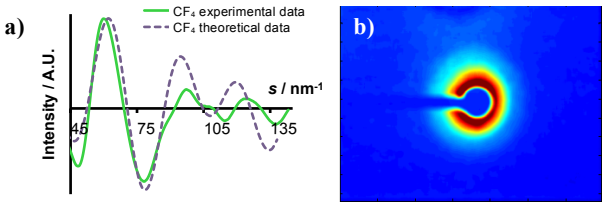

Figure 6: a) Comparison between theoretical and experimental diffraction data for CF_4, and b) diffraction pattern from a CF_4 molecular beam, pulsing at 50 Hz.

Following this proof of concept, we attempted to collect diffraction data for a sample of CCl_4 using a helium carrier gas, as it would be more representative of future experimental conditions. The acquired data are shown in Figure 7.

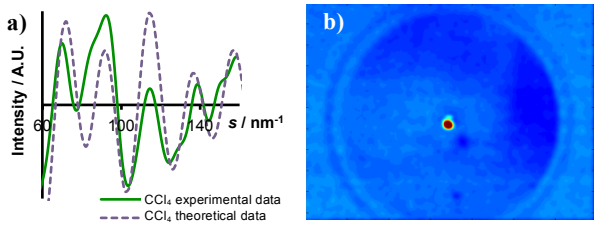

Figure 7: a) Comparison between theoretical and experimental diffraction data for CCl_4, and b) diffraction pattern from a CCl_4 molecular beam, pulsing at 50 Hz.

The detection of diffraction data for both CF_4 and CCl_4 was successfully achieved despite using nearly 300,000 times fewer electrons than a conventional gas electron diffractometer.

Future outlook

Following the successful detection of time-averaged gas electron diffraction and the major improvements made in the detector assembly, work is progressing towards designing a new nozzle system capable of supersonically cooling gas sample, and pulsing the molecular beam at a repetition rate similar to that of the probe electron beam. The end goal of this system is to use the laser's signal delay generator to trigger the pulse nozzle, magnetic lens and CCD camera in a concerted manner. Such developments will allow time-resolved gas electron diffraction to be performed in the near future.

A new sample holder for solid-state samples is currently being built, which will enable us to explore the technicalities associated with time-resolved experiments in a more familiar substrate, by performing time-resolved electron diffraction experiments upon melting a sample of polycrystalline platinum.

Future gas-phase time-resolved experiments will most likely include the study of dimethyl disulfide photodissociation using excitation with 266 nm light.

Acknowledgements

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