

DIFFRACTIVE IMAGING OF LASER INDUCED MOLECULAR
REACTIONS WITH KILOELECTRON-VOLT ULTRAFAST ELECTRON
DIFFRACTION

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DIFFRACTIVE IMAGING OF LASER INDUCED MOLECULAR REACTIONS WITH KILOELECTRON-VOLT ULTRAFAST ELECTRON DIFFRACTION

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Capturing the structural changes during a molecular reaction with ultrafast electron diffraction (UED) requires a high spatiotemporal resolution and sufficiently high signal-to-noise to record the signals with high fidelity. In this dissertation, I have focused on the development of a tabletop gas phase keV-UED setup with a femtosecond temporal resolution. A DC electron gun was employed to generate electron pulses with a high repetition rate of 5 kHz. The space charge effect in the electron pulse was ameliorated by compressing the 90 keV electron pulse longitudinally with a time varying electric field in an RF cavity. The velocity mismatch between electron and laser pulses was mitigated using a tilted laser pulse with an incident angle such that longitudinal component of the laser velocity is matched to the speed of electron pulse. The combination of these two techniques enabled the setup to reach a temporal resolution of 240 fs, more recently ~ 200 fs, and a timing drift of 50 fs rms over several hours. The UED was used to capture the laser induced alignment of linear and nonlinear molecules. The high beam current and femtosecond resolution allowed us to extract the molecular orientation distribution (MOD) of the molecular ensemble with high fidelity as it evolved from the prompt alignment to the past multiple revivals. To retrieve the MOD of nonlinear molecules, I developed a theory that

maps the MOD to the atom-pair angular distributions. The retrieval method does not require solving Schrödinger equation and works for any alignment methods. We also investigated ionization, fragmentation and isomerization of toluene generated by an IR strong laser field. Combined with the time-of-flight mass spectrometry, UED can determine the structure and yield of cations. A comparison of measurements to scattering calculations shows that scattering computation with independent atom model is inadequate to describe electron scattering from cations, and *ab-initio* calculation is required. Finally, the molecular photodissociation experiments with CF₃I and iodobenzene induced by a UV pulse were demonstrated with the keV-UED.

DEDICATION

To Haiyan Yu, my beloved wife,

and my children

PREVIEW

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Chapter 1

Introduction to ultrafast electron diffraction

1.1 Introduction

Electron and X-ray diffraction are powerful techniques used to investigate the microscopic world on the atomic scale [1], and both have a similar history of development with respect to technology and theory. The X-ray diffraction technique has been used to determine the three-dimensional structures of samples, ranging from crystals, to DNA and complex proteins, with atomic resolution since the beginning of 20th century [2, 3]. These major advances have enabled us to observe the static features or time-varying behaviors in molecules. Historically, the wave nature of electrons was first postulated by de Broglie in 1924, stating that all matter particles behave as waves and therefore can be diffracted [4]. The hypothesis was experimentally verified by the discovery of electron diffraction by Davisson and Germer using a crystal of nickel [5], and by Thomson and Reid using a thin film of celluloid [2, 6]. The discovery of electrons behaving as waves with wavelengths much shorter than the visible light opened up new opportunities to investigate the microscopic world of molecules where conventional microscopes were not able to. The first gas-phase electron diffraction (GED) was developed by Mark and Wierl to investigate the structure of CCl_4 in the 1930s [7]. Mourou and Williamson reported the first time-resolved electron diffraction experiment to probe a thin film of aluminum that demonstrates an electron pulse duration of 100 picoseconds (ps) generated by a streak camera in 1982 [8]. The first gas phase time-resolved electron diffraction experiments were conducted by synchronizing the electron pulses to either a microsecond laser pulse [9] or to a flash photolysis source [10] for the investigation of short-lived molecular species.

With the advent of femtosecond laser technology in the early 1990s, Zewail's group improved the temporal resolution of gas phase ultrafast electron diffraction (UED) into the picosecond regime [11-15], opening up new possibilities to study dynamics of molecules in real time. The pioneering works from Zewail's group achieved a series of groundbreaking UED results to capture the transient states of excited, isolated molecules with picosecond temporal resolutions. However, only slow immediate molecular states could be observed due to the limited temporal resolutions of their UED instrument. In these experiments, ultrafast laser pulses are used to both pump the sample and to produce the electron pulses to probe the sample. This idea has been considered as a standard methodology for the following development of UED setup.

In order to investigate atomic motion during a photoexcited chemical reaction, an overall temporal resolution of ~ 100 femtoseconds (fs) is required [16]. Recently a few techniques have been developed to achieve this goal, including compact setups [17, 18], relativistic electrons [19-21], electron pulse compression with radio-frequency (RF) fields [22, 23], tilted laser pulse [24, 25], *etc.* Gas phase UED experiments using megaelectron-volts (MeV) electron pulses have demonstrated a temporal resolution of 150 fs [19, 20, 26-28]. However, operating at the high energies requires a significantly larger infrastructure [26], and repetition rate and beam current are limited. For a sub-relativistic UED instrument, the RF compression technique has been developed to successfully compress electron pulses [22, 23, 29] to obtain an electron pulse duration of 150 fs [23]. The extra challenge of sub-relativistic, gas phase UED is that the velocity mismatch between the electron and laser pulses significantly deteriorates the overall temporal resolution [30]. The technique of tilted laser pulse has demonstrated the feasibility for compensating the velocity mismatch

in sub-relativistic electron diffraction [24, 25, 31, 32]. The combination of RF compression and tilted laser pulse techniques has allowed an overall temporal resolution of 240 fs for our sub-relativistic UED [32].

1.2 Motivations and thesis content

Recently, tremendous efforts have been devoted to improving the temporal resolution of gas phase UED instruments, mostly transitioning from kiloelectron-volt (keV) UED instruments [33-35] to relativistic MeV-UED [36-39]. However, these developments have not been able to increase the electron beam current significantly, which has been a limiting factor in gas phase UED experiments. The first application of a MeV-UED setup in a gas phase experiment has achieved a temporal resolution of 230 fs [19] and more recently 150 fs [40], compared to 240 fs for the gas phase keV-UED setup [32]. Low electron beam current has been the main limitation of gas phase MeV-UED, resulting in low signal levels and long acquisition times. Due to the presence of noise and timing instability that increases with time, low signal levels in many cases cannot be compensated by further increases the integration time. Furthermore, the limited beam time that is available to users has also been a major challenge, which has so far prevented systematic studies, i.e., exploring the wavelength dependence of the reaction dynamics and carrying out a set of experiments on similar molecules [32]. These systematic studies are essential to the understanding of the general mechanisms underlying photo-chemical reactions. One of the possible solutions is to develop a tabletop keV-UED setup with a higher electron beam current and a temporal resolution that is comparable to that of MeV-UED. Our first stage of experimentation has demonstrated a temporal resolution of 240 fs [32], more recently ~ 200 fs, for the gas phase keV-UED with an electron beam current that is more than an order of magnitude higher

than that obtained at MeV-UED facilities. The instrumental temporal resolution could be further improved by increasing the stability of the laser, RF system and tuning the parameters of the table-top setup.

The content of this thesis is organized as follows. In the chapter 1, I will give a brief introduction to ultrafast electron diffraction and the theory of electron scattering from a single molecule, including elastic and inelastic scattering, and then present the typical formulas for electron diffraction from a molecular ensemble and for molecular structure retrieval. In chapter 2, I demonstrate the electron pulse compression and tilted laser pulse techniques to improve the temporal resolution of the keV-UED. By combining these two techniques, the keV-UED has achieved a temporal resolution of 240 fs and a timing drift of 50 fs RMS for several hours, which is comparable to state-of-the-art facilities such as the MeV-UED setup at SLAC [32]. In chapter 3, I give a brief review of the theory of nonadiabatic alignment of molecules induced by an ultrafast laser pulse, and then demonstrate the theory to retrieve the molecular orientation distribution from atom-pair angular distributions. Also, I present in this chapter the theory to extract the angular distribution and internuclear distance of atom pairs with the UED measurement. In chapter 4, I show the rotational dynamics of impulsive molecular alignment, including linear and symmetric molecules, induced by a femtosecond laser pulse. Thanks to the high electron beam current, the keV-UED demonstrates the ability to capture a continuous temporal evolution of rotational dynamics of nitrogen with high fidelity and short acquisition times. We use the fast rotational dynamics of nitrogen to characterize the temporal resolution and timing drift of the setup. Also, we are able to retrieve the molecular orientation distribution for nonlinear molecules from experimentally measured atom-pair angular distributions,

which is demonstrated using rotational dynamics of trifluoro-iodomethane (CF_3I). In chapter 5, I demonstrate an ultrafast electron diffraction experiment from ions induced by a near infrared strong laser field. Combined with mass spectroscopy, UED can differentiate structures, including isomers, and determine the yield of products from ionization and fragmentation. In chapter 6, I demonstrate the preliminary experimental results of molecular dissociation dynamics induced by ultrafast UV pulses and captured by the keV-UED.

1.3 Principles of ultrafast electron diffraction

Electrons with wavelengths that are shorter than those of visible light can be easily obtained, allowing imaging devices with electrons to produce images with higher resolution than standard light microscopes. The first electron microscope was designed and built by Ernst Ruska in 1933 using a magnetic coil as a lens for electron beams [41]. The device provided a spatial resolution which far surpassed previous resolution capabilities and allowed scientists to observe things that cannot be seen with a light microscope [42]. Electrons behave as particles as well as waves due to the wave-particle duality. The wavelength of an electron is given by de Broglie's equation as

$$\lambda = \frac{h}{p}, \quad (1.1)$$

where h is Planck's constant, $p = \gamma m_e v$ is the electron momentum, $\gamma = 1/\sqrt{1 - v^2/c^2}$ is the Lorentz factor, m_e is the rest mass of an electron, v the velocity of the electron, and c the speed of light in vacuum. After being accelerated in an electric potential U , the total energy of the electron is given by

$$E = m_e c^2 + eU = \sqrt{p^2 c^2 + m_e^2 c^4}, \quad (1.2)$$

where e is the charge of an electron. Using the above two equations, the de Broglie wavelength is

$$\lambda = \frac{hc}{\sqrt{eU(2m_e c^2 + eU)}}. \quad (1.3)$$

For $U=0.1$ kV, the wavelength of electron $\lambda= 1.2$ Å, and for $U=90$ kV, $\lambda= 3.9$ picometers (pm).

Electron diffraction is a phenomenon resulting from the interaction between electrons and The potential of isolated molecules or atoms in crystalline materials, producing an interference pattern that characterizes the sample [43]. Unlike electron microscopy, UED instruments use coherent diffractive imaging (CDI), which is a lensless technique. The electrons scattered by the object generate a diffraction pattern which is recorded by a detector. The diffraction pattern is not a direct image of the object, but the information of the object is encoded in the pattern. We can use the classical Thomas Young's double slit experiment as an analogy to the electron diffraction experiment. The information, such as the wavelength of illuminating light, the width of the slits, and the distance between the slits are all encoded in the interference pattern. The width and distance can be successfully retrieved given the wavelength of the light. In a similar manner, electron diffraction patterns can be used to analyze objects which cause the diffraction. The advantage of CDI is that the diffraction pattern is aberration-free, and its spatial resolution is only determined by wavelength and electron beam quality, and not by the optics [44]. Thus, the CDI technique has been applied to probe ultrafast dynamics with high spatiotemporal resolutions [45].

Capturing the structural changes during a chemical reaction had been a challenge since it requires both a high spatiotemporal resolution on the order of sub-Angstroms and femtoseconds, and a sufficiently high signal-to-noise ratio to record the transient dynamics with high fidelity. Thanks to the advent of femtosecond laser technology, we are able to capture the ultrafast dynamics inside matter with experimental techniques, such as ultrafast X-ray diffraction and UED experiments, based on the combination of diffractive imaging and pump-probe spectroscopy. In the case of UED, a femtosecond laser pulse is split into two laser pulses, one of which is to excite the sample as a pump pulse, generating a non-equilibrium state, and the second one is used to first produce an electron pulse and then to probe the pump-induced changes in the sample. Each probe takes a snapshot of the transient state of the sample and the changes are measured as a function of time delays between the arrival time of the pump and probe pulses. When the overall temporal resolution is shorter than the intrinsic time scale of the change in the sample, the pump-induced dynamics can be captured accurately.

Recently, multiple experimental techniques have been developed to observe the change of molecular structures, such as Coulomb explosion imaging [46, 47], ultrafast X-ray diffraction [48-51], gas phase ultrafast electron diffraction (UED) [20, 21, 52-55], and laser-induced electron diffraction [56, 57]. The methods of diffractive imaging are directly sensitive to the spatial distribution of the constituent atoms of the molecule. In particular, UED has unique advantages compared to X-ray diffraction, as follows [2]. First, X-ray photons are scattered by the electron distribution through Thompson scattering, whereas UED electrons are scattered by both the nucleus and the electrons of the molecule through Coulombic interactions [2]. The cross section of electron scattering is about six orders of

magnitude stronger than that of X-ray scattering [34, 58], resulting in a much shorter exposure time for electron scattering. Second, electrons as a probe cause less damage to the sample being studied per useful scattering event. In each inelastic scattering event, the energy deposited to the sample using 1.5 Å X-ray photons is 400 times more than that of electrons, and the energy deposited in each useful elastic scattering event is 1000 times less for 80 to 500 keV electrons [2]. Third, due to the short penetration depth, electrons are suitable for experiments with gas phase targets, thin film samples, and surface characterization [2]. Fourth, tabletop UED instruments can be made through combination with ultrafast laser sources.

1.4 Theory of electron scattering

We start in this section with a description of elastic electron scattering from a potential with the first-Born approximation and briefly review the theory of correction of atomic form factors. We then show the total and inelastic scattering cross section from a single molecule in terms of charge density (or wave functions) by using the scattering matrix and the Morse approximation. Lastly, we show the analytic formalism of diffraction from a molecular ensemble, based on independent atom model, and the theory of retrieving the structural parameters.

1.4.1 Elastic scattering from a potential

The interaction between the probe electrons and the object of interest is through Coulomb interaction. Here, we give a brief review of the theory of electrons scattered elastically by a potential. *The following derivation follows the descriptions in ref.* [43, 59-62]. For an incident electron accelerated to 90 keV, the speed of the electron is $\sim 0.53 c$. Thus, the