## Chapter 1. Introduction

Time-resolved gas phase electron diffraction, or ultrafast electron diffraction (UED), as the state of the art is known today, permits the study of isolated molecular dynamics through direct determination of the structures involved. UED can be thought of as a pump-probe technique, but where spectroscopists might use a light pulse to monitor a specific state, instead in UED an electron pulse diffracts from the mixture of ground and excited molecules. Unlike most spectroscopic methods, diffraction is sensitive to all structures within the path of the electron beam regardless of their light-emitting properties. In fact, radiationless transitions in molecules are common following electronic excitation and by definition involve non-emitting species. Such "dark" structures may be resolved by diffraction and are a particular focus of this work.

## **1.1 Historical perspective**

The evolution of conventional gas electron diffraction (GED) into modern timeresolved electron diffraction has been reported on by other authors.<sup>1</sup> Time-resolved electron diffraction itself, however, has been a topic of research for over two decades. It was grown through the combination of conventional GED and pump-probe spectroscopy, with each method lending its advantages to the blossoming field. One of the earliest experiments aimed at structural characterization of transient species simply used a continuous electron beam with a stroboscopic shutter to produce microsecond pulses. The trifluoromethyl radical (CF<sub>3</sub>) was identified following multiphoton photolysis of trifluoromethyl iodide (CF<sub>3</sub>I) by infrared radiation.<sup>2</sup> Similarly, the fragmentation of chlorine dioxide (ClO<sub>2</sub>) was studied with 100 µs electron pulses in 1984.<sup>3</sup> These studies were qualitative, identifying the radical products without a comprehensive structural analysis nor extracting any information on dynamics. Major development in the field occurred with the incorporation of digital detecting systems (at first, a photodiode array) into electron diffractometers such that data could be obtained in real time with the experiment, and multiple time-resolved data points (with respect to the delay between an excitation laser pulse and a probe electron pulse) could be recorded easily.<sup>4</sup>

Time-resolved gas electron diffraction on the nanosecond to microsecond time scale was introduced in early 1990s in the labs of Ewbank and Schäfer.<sup>5,6</sup> These experiments were the first direct quantitative structural work on a photochemical reaction. At the same time, though, UED was being developed in the Zewail labs at Caltech<sup>7,8</sup> and elsewhere (see Refs. 9 and 10). Shortly after the report of nanosecond

time-resolved electron diffraction results of the 193 nm radiation-induced fragmentation of carbon disulfide (CS<sub>2</sub>) by Ewbank *et al.*,<sup>5</sup> the first qualitative data on the fragmentation of CF<sub>3</sub>I with picosecond electron pulses was presented by Williamson *et al.* at Caltech.<sup>11</sup>

From these early experiments, the UED method forged ahead thanks to the pioneering work by the researchers at Caltech. Two generations of UED apparatus followed the first and a number of significant photochemical and photophysical problems were studied and solved.<sup>8</sup> The first quantitative structural information reported by UED was for the products of dissociation of iron pentacarbonyl [Fe(CO)<sub>5</sub>]. In this study, the parent molecule was found to fragment within 10 ps into products iron dicarbonyl [Fe(CO)<sub>2</sub>], iron carbonyl (FeCO), and atomic iron. The radical structures and product branching ratio were determined.<sup>12</sup> Using the picosecond electron pulses, UED was also able to establish the experimental time scale for the iodine elimination reaction from 1,2-diiodotetrafluoroethane (C<sub>2</sub>F<sub>4</sub>I<sub>2</sub>). The intermediate (C<sub>2</sub>F<sub>4</sub>I) in this non-concerted reaction was qualitatively identified as having the classical structure – the remaining iodine atom is bound to one carbon only and not bridged across them.<sup>13</sup>

The non-concerted elimination of iodine atoms from  $C_2F_4I_2$  was revisited upon the construction of the third generation of ultrafast electron diffraction apparatus. With the increased sensitivity garnered by this development the intermediate was confirmed to be of classical structure and the geometrical parameters themselves were refined.<sup>14</sup> The loss of the first iodine atom was found to occur before 5 ps and the loss of the second in 26 ps. This improved apparatus also allowed for the first UED study on a molecular system that lacks heavy atoms (i.e., composed of no atoms beyond the second row of the periodic table, the significance of this will be made clear later). Cyclohexadiene ( $C_6H_8$ ) was observed to open its ring and form hexatriene; the structural parameters and time constant of formation was determined.<sup>14,15</sup>

Further work with UED continued to explore the structural dynamics of photophysical and photochemical processes of compounds lacking heavy atoms, the sensitivity of the machine improved beyond that of its predecessors enough to make this feasible. The coupling of high-level theoretical calculations to results of UED was also increased and permitted systematic study of possible structural pathways and detailed explanations of the dynamics of the complex potential energy surfaces. Hence the nature of spectroscopically dark structures becomes accessible.

## 1.2 This thesis

Within the following chapters the application of UED to fundamental photophysical and photochemical excited state processes is described. Space is granted for a thorough account of the theoretical and experimental methodology that makes this all possible. The details of diffraction pattern acquisition and their processing into the analyzable data used to extract molecular structures is of particular focus as developments in this area have occurred since the third generation of UED was introduced years ago. The experimental results of the application of UED to ground state diffraction problems as well as several excited-state problems are reported and explained.

Chapter 2 gives a brief overview of the theory of gas electron diffraction. For the subsequent chapters an understanding of the basics of electron diffraction is necessary,

but the exhaustive details are not and have been dealt with by other authors numerous times in the past. Chapter 3 introduces the UED experimental apparatus and proceeds to present an explanation of each of its component parts. This chapter also treats important experimental issues unique to UED, such as beam pulse widths, clocking and time zero, velocity mismatch between laser and electron pulses, and the overall time resolution. Chapter 4 may be the most important of the chapters. It explains the process by which the signal from scattered electrons as collected on the digital detector becomes the structure of a transient species. Here is presented the theoretical methodology used by the UED researcher to manage the graphical data and unite the UED results with the theory that has served conventional gas electron diffraction (GED) for so many years. A treatment of the quantum chemical calculations by which the structural dynamics may be further explored is also included as are some comments on the programs used for molecular structural refinement.

Chapter 5 begins the results section of this thesis. The ground state diffraction data for a number of molecules is reported and the results of structural refinement explained. Here is provided a comparison between the diffraction of molecules containing heavy atoms and those without. This chapter also provides a valuable comparison between the structures determined by UED and the structures of the same molecules as determined by prior conventional GED groups. Two ground-state molecular structures are reported here for the first time. Chapter 6 moves on to the results of the time-resolved diffraction study of acetylacetone upon ultraviolet excitation. The fragmentation reaction is witnessed to occur to the exclusion of other theoretically possible pathways. The products of the reaction are structurally resolved and the time constant of their formation determined. An intermediate structure in this reaction is qualitatively recognized.

The desire to study excited-state structures is realized in Chapter 7 with the account of the UED studies on the aromatic carbonyl molecules benzaldehyde and acetophenone. Here, a bifurcation of pathways from the excited state is discovered. One pathway leads down a chemical channel to dissociation products and the other along a physical channel to a long-lived excited state. The excited state is structurally very different from the ground state which allows for its electronic character to be identified. Although the physical channel is the same for both aromatic carbonyls, the chemical channel differs between benzaldehyde and acetophenone. In benzaldehyde the presence of the aldehydic hydrogen opens up a dissociation pathway that is dependent on the large amplitude motion of this light atom. In acetophenone, the methyl group that has been substituted for the hydrogen undergoes no such motion and the chemical pathway is simple homolytic bond cleavage. The structures are determined and the time scales resolved. High-level quantum chemical calculations of the excited-state surfaces aid in the interpretation of the UED results and the explanation of the structural dynamics.

An appendix following the concluding remarks explains some approximations that are made in the theory of UED. It also includes source code for some of the critical functions contained within the data analysis software. The function code is accompanied by brief comments aimed at an explanation of their purpose.

## **1.3 References**

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