

Chapter 8.

Conclusions and Future Directions

8.1. Summary of results

The previous chapters held a detailed account of the state of the art of ultrafast electron diffraction. The experimental apparatus was described showing its breakdown into component parts. The UED machine is a combination of an amplified femtosecond laser system, high flux, high-vacuum molecular beam sample delivery, sensitive single electron digital detection, and an ultrafast pulsed electron gun – each element in itself representing an independent scientific achievement. However, the experiment is only as good as the theoretical methodology used to extract meaningful conclusions from the data. Chapter 4 described how, from the signal of electrons scattered off the molecular beam, the structural parameters and dynamics of complex molecular systems may be determined. Furthermore, the application of high-level theoretical calculations has revolutionized the interpretation of UED results. It has permitted the determination of

structural changes occurring along electronically excited-state decay pathways that had heretofore been inaccessible. It also permits the UED structural results to be directly compared to optimized geometries from these calculations providing a unique and useful benchmark.

Chapter 5 detailed experiments performed on several molecules using UED as a simple conventional gas-phase electron diffraction apparatus. The significance of this work is twofold. Most obviously, the structures of 2-fluoropyridine, acetophenone, and methylbenzoate were determined for the first time. Due to the low symmetry of 2-fluoropyridine and the size and complexity of the two aromatic carbonyl molecules, they were challenging test cases for diffraction experiments and showed how through creative use of structural constraints in the model used for refinement to the data, a geometry could be accurately determined. The second, and equally as meaningful, feature of these ground-state diffraction experiments is the comparison between the UED-determined molecular structures and those structures previously determined by renowned gas-phase diffraction groups. Such comparisons not only justify UED as a powerful structural tool but also burgeon confidence in the structures determined for transient species.

The structural dynamics of acetylacetone as described in Chapter 6 is an ideal introduction into the determination of excited state structures. In this experiment the structures of the products of a straightforward reaction, the elimination of hydroxyl radical from acetylacetone, were determined. In addition to the reaction kinetics, observed through analysis of the time-resolved images, the dynamics of the reaction were also pieced together through cooperation between experimental and theoretical methods.

A structure consistent with that of an excited singlet state of acetylacetone was found at early time points and seen to decrease as the amount of radical product structures increased.

This introduction to excited-state structure was followed up by experiments on benzaldehyde. The decay of excited state benzaldehyde was found to undergo a bifurcation into photochemical and photophysical pathways. The photochemical pathway produced benzene and carbon monoxide. This reaction involved an intramolecular hydrogen shift before the carbonyl moiety could detach. Calculations on the excited state surface found that, on S_1 , the aldehydic hydrogen atom had a much lower energy for wagging. This large-amplitude motion permitted its capture by the primary carbon of the aromatic ring. An intermediate state formed where the hydrogen and carbonyl group were both bound and from which benzene and carbon monoxide both formed in the ground states when the carbonyl group departed. Also from S_1 , the photophysical channel resulted in a structure that was refined and found to be consistent with that of the $\pi\pi^*$ T_2 state of benzaldehyde. This was the first excited-state structure ever determined by electron diffraction. The structure of this excited state proved to be interesting in that the aromatic ring was quinoid with two double bonds and four single bonds as one would expect where aromaticity is lost in such a $\pi\pi^*$ state.

The methodology was applied again in order to compare the processes of excited benzaldehyde with that of its related (methylated) congener acetophenone. Acetophenone was found to undergo a similar bifurcation into chemical and physical pathways from the S_1 state. However, the ketonic methyl group does not engage in low-frequency wagging

as the aldehydic hydrogen did on the benzaldehyde S_1 surface. It is not captured by the primary aromatic carbon and, hence, a molecular dissociation pathway does not take place. Instead the methyl group homolytically cleaves from the molecule producing radical products – benzoyl and methyl. But like benzaldehyde, intersystem crossing is an efficient process and the excited state T_2 of acetophenone is structurally resolved sharing with benzaldehyde a quinoid ring indicative of the $\pi\pi^*$ excitation.

The accomplishments of UED in the field of photochemistry and photophysics are profound. Never before have the dynamics of such “dark” processes been explored by their direct structural determination. The continuation of UED studies on systems of physical chemical interest promises further surprises and each discovery broadens our understanding of the excited state behavior of isolated molecules.

8.2. Developments and future directions

Since the lab at Caltech is the only experimentally active gas-phase UED facility in the world, the potential for development is vast. One must then regard potential development as either an improvement of the existing experiment or striking a new direction entirely. Considering UED, developments of either sort will likely be focused on one of the disparate experimental units – electron generation, laser excitation, and the sample. Each will be addressed individually.

8.2.1. The sample

As noted in Chapter 3 progress has been made in making the sample inlet more versatile, e.g., a manifold of all-metal construction has been implemented such that

compounds of a high boiling point may be studied in the beam. However, issues remain, and UED continues to be limited by the sample. During the course of an experiment at least 100 mL of liquid sample is expended, 200 mL or more in a typical experiment with about 20 time-resolved data points. This limits the compounds of study to those that are inexpensive and readily available. This situation may be remedied by incorporating a pulsed valve into the molecular beam delivery tube. Since the experiment itself is pulsed at 1 kHz, orders of magnitude less sample could be used if such a scheme were employed. However, two issues would have to be addressed – field contamination by the valve switch and molecular density. Field contamination has been relieved by Bartell with techniques of shielding and pulse timing that could also be applied, in principle, in UED.¹ Molecular density poses a more difficult problem to master in that a lower number of molecules translates to lower scattering signal unless more electrons are added to each pulse – thereby exacerbating space-charge effects and broadening the experimental time resolution. If a properly shielded, 1 kHz pulsed nozzle with a sufficient flux can be obtained, a host of new compounds will become available for study with UED.

The recent implementation of the high-temperature nozzle system brings about another problem – many molecules, particularly those organic compounds that have been of interest previously, are not thermally stable at high temperatures. Attempted experiments on uracil that coated the inlet system with charcoal serve as evidence of this limitation. The desire to experiment on such samples that are not thermally stable has fostered the birth of a new generation of gas-phase ultrafast electron diffraction. Using the sample delivery technique of laser desorption, solid sample will be directly vaporized

by its thermally mediated expulsion from a graphite surface. The ejected molecules form a molecular beam immediately after their desorption and are then exposed to the pulsed excitation laser and electron pulses that are common to UED as described in Chapter 3. This new combination of techniques will not only permit solid samples of dubious thermal stability to be experimented upon but will also expand the breadth of samples into those of biological importance – peptides and nucleotides and their kin. The pulsed nature of desorption requires the small amount sample that is the standard when obtaining biological compounds.

8.2.2. The laser

Laser excitation in UED is, and has been, at 266.7 nm only. Photons of this same energy are also used to generate electrons after the initial amplified pulses are split. This naturally limits the molecules being studied to those that have strong absorptions at 266.7 nm. Fortunately, finding systems that absorb in the far UV is not difficult. Tunability, however, would open up more possibilities – particularly if the photon energy could be raised into the vacuum UV where all molecules absorb strongly (generating electron pulses at this wavelength would also be straightforward). Such high-energy excitation often populates dissociative states allowing UED to study many sorts of fragmentation reactions.

Although UED does use linearly polarized light, effects of the polarization, such as anisotropy of the excited sample, have never been observed. However, techniques of high-field alignment, rotational coherence, and molecular beam anisotropy in diffraction

have been, at least to first order, studied theoretically² and experimentally.³ The possibility remains for a thorough exploration of these phenomena using UED.

8.2.3. Electron generation

UED is an experiment in the picosecond time regime. Electron pulses containing a sufficient number to perform an experiment (~25,000 electrons/pulse) typically have a pulsewidth of a few picoseconds. The electron gun, however, is capable of shorter pulse generation as can be seen from the plot in Fig. 3-12. The experimental usefulness of these ultrashort pulses is dubious for several reasons – first, as previously mentioned, is the electron flux, which dictates how long the experiment must continue (to collect images for averaging) to achieve adequate signal to noise. Second is the benefit of shorter pulses. Even with femtosecond electron pulses the overall time resolution of the experiment is governed by the velocity mismatch between excitation laser pulses and electron pulses within the molecular beam. Fig. 3-15 is quite clear in its depiction of this effect. However, the situation may be remedied if the electrons are accelerated to speeds closer to the speed of light and the width of the molecular beam (the interaction region) is shrunk, thereby decreasing the path length where the mismatch occurs.

Methods for accelerating electrons are widespread in diffraction and microscopy. In the simplest solution, the electron gun as it is currently in UED is simply exposed to a higher extraction field. Although seemingly convenient it has the disadvantage of making the gun even more susceptible to arcing problems than it is already. Furthermore, the extraction field cannot be raised to a value much higher than it is now since some

preliminary tests of this with the UED apparatus have experienced voltage breakdown. An alternative would be an entirely new design, such as a tip as used in electron microscopy, where electron pulses containing orders of magnitudes less electrons are created with an orders of magnitude higher repetition rate. This satisfies both the ultrashort temporal pulsewidth and the need for a sufficient total electron flux. Problems may arise due to the speed of molecules in the molecular beam (refresh rate) and the energy of excitation laser pulses needed, but these are technical problems and may be surmounted at some point in the future. Femtosecond electron pulses will, of course, open up the world of ultrafast dynamics to UED and perhaps allow, for the first time, the direct structural resolution of periodic coherent nuclear movement.

In the other direction, a different sort of information would become more readily accessible if instead of shortening the electron pulses, they were broadened. Rather than using the back-illuminated electron gun as employed in UED, a front-illuminated Pierce-type gun could be used,⁴ which is known to provide orders of magnitude more electrons per pulse – at the expense of temporal pulsewidth. Such a scheme is advantageous for certain experiments where structural determination is more important than kinetics and dynamics. For instance, the product structures reported in Chapters 6 and 7 need not have been determined from data taken using picosecond electron pulses. Furthermore, higher electron flux would cut down on the operational time for the experiment reducing the amount of sample used and allowing more experiments on different systems in the same time period. Higher electron flux also (see above) permits experimentation on samples

with low molecular density in the gas phase opening up countless new opportunities for discovery by UED.

8.3 References

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