Structural Dynamics of Complex Molecules
by Ultrafast Electron Diffraction:
Concepts, Methodology and Applications

Thesis by
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Dedicated with love and gratitude
to
Bhagawan Sri Sathya Sai Baba
and to
my dearest parents
Aruna and N.V. Srinivasan
Acknowledgements

In my native land of India, every person is regarded as having two births—the first, birth into the physical world, and the other, birth into the world of knowledge. Indian tradition emphasizes that for the former birth, we are eternally indebted to our parents, and for the latter, we are ever beholden to our teacher. It is in that spirit of my ancestors that I write these words of gratitude to my teacher and mentor, Prof. Ahmed Zewail. The human language, while a wondrously marvelous gift, often fails at times such as these to adequately express the whole gamut of one’s emotions. Yet, standing as I am at the end of a long and arduous period of graduate school, it is but natural that I seek to acknowledge his profound influence on my growth as a scientist and as a human being. My entry into the Zewail group came about under very unusual circumstances, the details of which will have to wait for another day. Over the course of my studentship, I have been struck and inspired by his passion for science and his insatiable curiosity about the natural world. The award of the Nobel Prize in 1999 was certainly one of the high points of my tutelage under him. I am reminded of an anecdote that Isidor Isaac Rabi once shared, “My mother made me a scientist without ever intending to. Every other Jewish mother in Brooklyn would ask her child after school, ‘So? Did you learn anything today?’ But not my mother. ‘Izzy,’
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Abstract

The central theme in ultrafast electron diffraction (UED) is the elucidation of the structural dynamics of transient molecular entities. With properly timed sequences of ultrafast electron pulses, it is now possible to image complex molecular structures in the four dimensions of space and time with resolutions approaching 0.01 Å and 1 ps, respectively. Reaching this spatiotemporal resolution on the atomic scale has been the driving force behind the development and application of the third generation UED instrument—the subject of this dissertation. The current state-of-the-art in resolutions and sensitivity, together with theoretical advances, has made possible the direct determination of transient structures, leading to studies of diverse molecular phenomena hitherto not accessible to other techniques. By freezing structures on the ultrafast timescale, we are able to develop concepts that correlate structure with dynamics. Examples include structure-driven radiationless processes, dynamics-driven reaction stereochemistry, and non-equilibrium structures exhibiting negative temperature, bifurcation, or selective energy localization in bonds. These successes in the studies of complex molecular systems, even without heavy atoms, establish UED as a powerful method for mapping out temporally changing molecular structures in chemistry, and potentially, in biology.
Table of Contents

Acknowledgements ................................................................. iv
Abstract ......................................................................................... viii
List of Figures ................................................................................. xiv
List of Schemes ................................................................................. xxiii
List of Tables .................................................................................... xxiv

1. Introduction ................................................................................... 1
   Figures ......................................................................................... 10
   References ................................................................................... 12

2. UED Theory .................................................................................. 18
   2.1 Introduction ............................................................................. 18
   2.2 The Diffraction-Difference Method: Transient Structures........... 22
   2.3 Ground-State Structures ........................................................ 27
   2.4 Structure Search and Refinement .......................................... 28
       Figures ..................................................................................... 32
       References ............................................................................. 35

3. Third Generation UED Instrumentation ...................................... 36
   3.1 Introduction ............................................................................ 36
   3.2 Femtosecond Laser System .................................................. 37
   3.3 Vacuum Chambers and Molecular Beams .............................. 39
   3.4 Electron Gun .......................................................................... 40
   3.5 CCD Camera System ............................................................ 41
   3.6 Time-of-Flight Mass Spectrometer ...................................... 44
       References ............................................................................. 45
       Figures ..................................................................................... 46
6. Dark Structures in Nonradiative Processes
   6.1 Introduction
   6.2 Ground-State Structures
      A. Pyridine
      B. 2-Picoline
      C. 2,6-Lutidine
   6.3 Transient Structures
      A. Pyridine
      B. 2-Picoline
      C. 2,6-Lutidine
   6.4 Photochemistry
      A. Pyridine
      B. 2-Picoline
      C. 2,6-Lutidine
   6.5 Photophysics
   6.6 Conclusions

7. Non-Equilibrium Structures
   7.1 Introduction
   7.2 Concepts of Equilibrium vs. Non-equilibrium Structures
   7.3 Experimental Methodology
   7.4 Data Processing and Analysis
      A. Background Subtraction
      B. Generation of “Product-Isolated” Curves from Diffraction
         Difference Signals
      C. Novel Aspects of the Product Structure Analysis Used for
         “Hot” HT Product

References
9. Hydrogen-Bonding in Acetylacetone
   9.1 Introduction
   9.2 Experimental
   9.3 Ground State
   9.4 Structural Dynamics
   9.5 Results and Discussion
   9.6 Conclusions

10. Conclusions and Future Directions
    Figures
    References
List of Figures

1-1  Example of diffraction with two scattering centers................................. 10

1-2  The UED experiment......................................................................................... 11

2-1  Concept of ultrafast electron diffraction......................................................... 32

2-2  The diffraction-difference method................................................................. 33

2-3  Isolation of transient species through choice of $t_{ref}$................................. 34

3-1  Third-generation UED-3 apparatus............................................................... 46

3-2  Layout of beam path for the femtosecond laser pulses ............................... 47

3-3a Schematic front view of the UED-3 apparatus............................................ 48

3-3b Schematic side view of UED-3 apparatus................................................. 49

3-4  Schematic of UED-3 electron gun assembly............................................... 50

3-5  Detailed view of the electron generation and acceleration
    assembly ........................................................................................................... 51

3-6  Equipotential lines in extraction region of electron gun......................... 52

3-7  Detailed view of magnetic lens assembly .................................................... 53
3-8  Detailed view of the electron streaking and deflection assembly .......... 54
3-9  UED-3 detector assembly ..................................................................... 55
3-10 Individual components of the custom-made detector assembly .......... 56
3-11 Photographs of selected detector components ....................................... 57
3-12 Schematic of time-of-flight mass spectrometry apparatus ................. 58
3-13 The linear TOF-MS chamber ............................................................... 59
3-14 Acceleration and detector assembly for time-of-flight apparatus ......... 60
3-15 Geometry of time-of-flight mass spectrometer ................................... 61
3-16 Arrangement and synchronization of electrical pulses in TOF-MS ...... 62
3-17 Typical mass spectrum obtained in the TOF-MS apparatus .............. 63
4-1  Calibration of electron gun via streaking experiments ......................... 92
4-2  Typical X-Y profile of the nearly circular electron beam .................... 93
4-3  Results of in situ streaking experiment for electron pulse measurement .................................................................................................................. 94
4-4  Calibration of electron pulse width ...................................................... 95
4-5  Improvement in electron gun performance .......................................... 96
4-6  Pulse-to-pulse stability of the electron gun ................................................. 97
4-7  Lensing experiment to determine in situ the zero-of-time ......................... 98
4-8  Photoionization-induced ‘lensing’ effect for measuring time-zero ............ 99
4-9  Geometry of crossed-beam experiment ...................................................... 100
4-10 Angular dependence of temporal broadening due to velocity mismatch .................................................................................................................. 101
4-11 Overall temporal resolution (including velocity mismatch) as a function of spatial and temporal width of the electron pulses .............. 102
4-12 Calibration of pixel size on phosphor screen using Group 0, Element 1 of the USAF-1951 resolution target ......................................................... 103
4-13 Determination of mean pixel size on phosphor screen ......................... 104
4-14 Modulation Transfer Function for the ICCD camera ......................... 105
4-15 Calibration of single electron events on the detector ............................ 106
4-16 Inverse atomic ratio method ................................................................. 107
4-17 Processing procedure for 2-D diffraction images and ground-state data analysis .................................................................................................... 108
4-18 Diffraction-difference analysis for time-resolved experiments ........... 109
LIST OF FIGURES

4-19 Divergence of electron beam.......................................................... 110

5-1 Ground-state molecular diffraction image of $\text{C}_2\text{F}_4\text{I}_2$ .................. 135

5-2 Refined ground-state structure of $\text{C}_2\text{F}_4\text{I}_2$................................. 136

5-3 Time-resolved 2D diffraction-difference images of $\text{C}_2\text{F}_4\text{I}_2$ .......... 137

5-4 Effect of Fourier filtering on raw diffraction-difference curves............. 138

5-5 Time-resolved structural changes in the elimination of iodine from $\text{C}_2\text{F}_4\text{I}_2$.......................................................... 139

5-6 Time-resolved structural changes involving only the $\text{C}_2\text{F}_4\text{I} \rightarrow \text{C}_2\text{F}_4 + \text{I}$ contribution to the diffraction-difference signal ................. 140

5-7 Time dependence of the formation of $\text{C}_2\text{F}_4$ molecules from the decay of $\text{C}_2\text{F}_4\text{I}$ transient structures ................................................. 141

5-8 Structural determination of the transient $\text{C}_2\text{F}_4\text{I}$ intermediate......... 142

5-9 Refinement of the $\text{C}_2\text{F}_4\text{I}$ radical structure........................................ 143

5-10 Complete structural determination of the $\text{C}_2\text{F}_4\text{I}_2$ elimination reaction .......................................................... 144

6-1 Ground-state molecular diffraction image of pyridine...................... 185

6-2 Comparison between experimental and refined theoretical $s\text{M}(s)$ and $f(r)$ curves for ground-state pyridine .................................................. 186
6-3  Refined ground-state structural parameters of pyridine................. 187
6-4  Ground-state molecular diffraction image of picoline..................... 188
6-5  Refined ground-state structural parameters of picoline .................. 189
6-6  Ground-state molecular diffraction image of 2,6-lutidine............... 190
6-7  Comparison of ground-state structures of the three azines ............. 191
6-8  Refined ground-state structural parameters of lutidine .................. 192
6-9  Time-resolved 2D diffraction-difference images of pyridine .......... 193
6-10 Time-resolved 1D radial distribution curves for pyridine ............. 194
6-11 Possible structures from reaction of pyridine ............................ 195
6-12 Comparisons of the experimental radial distribution curve with
      normalized theoretical curves for possible pyridine channels......... 196
6-13 Structural parameters of the pyridine ring-opened product .......... 197
6-14 Refinement of ring-opened pyridine structure ............................. 198
6-15 Pyridine structure and population change with time .................... 199
6-16 Temporal dependence of the pyridine product fraction ................. 200
6-17 Possible structures from reaction of picoline ............................. 201
6-18  Structural parameters for the picoline ring-opened product ............... 202
6-19  Temporal dependence of the picoline product fraction...................... 203
6-20  Time-resolved 1D radial distribution curves for lutidine ................... 204
6-21  Possible structures from reaction of lutidine...................................... 205
6-22  Comparisons of the experimental radial distribution curve with normalized theoretical curves for possible lutidine channels .............. 206
6-23  Lutidine structure and population change with time ......................... 207
6-24  Temporal dependence of the lutidine product fraction ...................... 208
6-25  Photochemistry of azines elucidated by UED.................................... 209
7-1   Calculated diffraction curves for a single bond in the equilibrium regime ................................................................................................................. 261
7-2   Calculated diffraction curves for a single bond in the non-equilibrium regime ........................................................................................................... 262
7-3   Observed ground-state diffraction image and corresponding f(r) curve for CHT ...................................................................................................... 263
7-4   Observed ground-state diffraction image and corresponding f(r) curve for CHD .................................................................................................. 264
7-5   Refined structural parameters of ground-state CHT ............................. 265
7-6 Refined structural parameters of ground-state CHD ....................... 266

7-7 Non-equilibrium ‘negative temperature’ in CHT as reflected in the transient-only sM(s) curves ................................................................. 267

7-8 Non-equilibrium ‘negative temperature’ in CHT .......................... 268

7-9 Evolution of transient non-equilibrium structure in CHT.............. 269

7-10 Time-resolved 2D diffraction-difference images of CHD ............... 270

7-11 Time-resolved formation of hot HT structures after CHD ring opening ................................................................................................. 271

7-12 Temporal evolution of hot HT structures following ring opening of CHD ............................................................................................... 272

7-13 Structural refinement of ring-opened HT structure ..................... 273

7-14 Evolution of transient far-from-equilibrium structure in CHD ....... 274

7-15 Potential energy landscape relevant to the formation of HT ......... 275

8-1 Diffraction of ground-state COT3 and BCO structures in thermal equilibrium .......................................................................................... 304

8-2 Ground-state molecular scattering curves for COT3 and BCO ...... 305

8-3 Ground-state radial distribution curves for COT3 and BCO .......... 306
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>8-4</td>
<td>Diffraction-difference images of light-mediated reaction of COT3</td>
<td>307</td>
</tr>
<tr>
<td>8-5</td>
<td>COT3 molecular scattering diffraction-difference curves</td>
<td>308</td>
</tr>
<tr>
<td>8-6</td>
<td>COT3 radial distribution diffraction-difference curves</td>
<td>309</td>
</tr>
<tr>
<td>8-7</td>
<td>Potential energy landscape for OT conformer structures</td>
<td>310</td>
</tr>
<tr>
<td>8-8</td>
<td>Refined transient-only OT structures</td>
<td>311</td>
</tr>
<tr>
<td>9-1</td>
<td>2D ground-state diffraction image of acetylacetone</td>
<td>332</td>
</tr>
<tr>
<td>9-2</td>
<td>Structural refinement of ground-state acetylacetone</td>
<td>333</td>
</tr>
<tr>
<td>9-3</td>
<td>Refined structural parameters of the AcAc enol tautomer</td>
<td>334</td>
</tr>
<tr>
<td>9-4</td>
<td>Observed structural dynamics of acetylacetone</td>
<td>335</td>
</tr>
<tr>
<td>9-5</td>
<td>Experimental and theoretical diffraction-difference data for different reaction pathways of acetylacetone</td>
<td>336</td>
</tr>
<tr>
<td>9-6</td>
<td>Refinement of “product only” data in acetylacetone</td>
<td>337</td>
</tr>
<tr>
<td>9-7</td>
<td>Refined structural parameters of the 2-penten-4-on-3-yl radical</td>
<td>338</td>
</tr>
<tr>
<td>9-8</td>
<td>Evolution of OH loss products for all experimental time slices</td>
<td>339</td>
</tr>
<tr>
<td>9-9</td>
<td>Difference-difference data to discriminate between singlet and triplet structures</td>
<td>340</td>
</tr>
</tbody>
</table>
9-10 Structures involved in the dynamics of the OH elimination reaction ......................................................... 341

9-11 Power-dependence studies of acetylacetone photochemistry .............. 342

10-1 Phenomena and concepts elucidated by UED ................................................. 351
List of Schemes

5-1 Non-concerted elimination reaction of \( \text{C}_2\text{F}_4\text{I}_2 \) with the hitherto unknown reaction intermediate............................................................ 133

5-2 Dihalide elimination reactions involving \( \text{C}_2\text{R}_4\text{X} \) radical intermediates......................................................................................... 134

6-1 Pyridine reaction with multiple reaction pathways................................. 184

7-1 Nonradiative decay of excited 1,3,5-cycloheptatriene to ‘vibrationally hot’ ground state............................................................. 259

7-2 Ring opening of 1,3-cyclohexadiene to form 1,3,5-hexatriene.............. 260

8-1 Thermal Cope rearrangement of 1,3,5-cyclooctatriene to bicyclo[4.2.0]octa-2,4-diene ................................................................... 301

8-2 Light-mediated electrocyclic ring opening of 1,3,5-cyclooctatriene to 1,3,5,7-octatetraene........................................................................... 302

8-3 Thermal equilibrium of 1,3,6-cyclooctatriene, 1,3,5-cyclooctatriene, and bicyclo[4.2.0]octa-2,4-diene ......................................................... 303

9-1 Structures of enolic acetylacetone................................................................. 330

9-2 Acetylacetone enol-keto tautomerization by hydrogen shift.................. 330

9-3 Possible reactions of acetylacetone following UV excitation............... 331
List of Tables

5-1  Experimental and theoretical values of structural parameters for the classical C₂F₄I radical intermediate.............................................................. 145

7-1  Refined structural parameters of the far-from-equilibrium HT structure ............................................................................................................. 276

8-1  Structural coordinates of COT3 obtained from least-squares partial refinement of UED data................................................................. 312