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"Femtosecond Real-Time Probing of energetic Reactions: Complex Organics and Advanced Techniques."

July 1997 – September 2004

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14. ABSTRACT

The research was focused on two major areas. The first area is the advancement of new techniques to elucidate elementary steps of reactions in complex molecular systems. In the second area, the effort was on the applications of these techniques to: (i) the studies of reactive intermediates of energetic reactions, and (ii) the dynamics of prototype molecular explosives. We have succeeded in advancing the new techniques for the studies of structure and dynamics of highly-excited and energetic molecules, and the progress in theoretical and experimental studies has been published in a series of papers.

15. SUBJECT TERMS

Probing of energetic molecules and reactions.

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ABSTRACT

The research was focused on two major areas. The first area is the advancement of new techniques to elucidate elementary steps of reactions in complex molecular systems. In the second area, the effort was on the applications of these techniques to: (i) the studies of reactive intermediates of energetic reactions, and (ii) the dynamics of prototype molecular explosives. We have succeeded in advancing the new techniques for the studies of structure and dynamics of highly-excited and energetic molecules, and the progress in theoretical and experimental studies has been published in a series of papers.

TECHNICAL SECTION (Including Objectives, Approach, and Progress)

Technical Objectives:

Three major areas of research represent the focus of this proposal. The first area is the advancement of new techniques to elucidate elementary steps of reactions in complex molecular systems. In the second area, the effort was on the applications of these techniques to: (i) the studies of reactive intermediates of energetic reactions, (ii) the dynamics of prototype molecular explosives, and the third area (iii) involves theoretical studies, ab initio, and molecular dynamics of complex organic reactions. We made major advances (see publications) in areas (i) and (iii), but did not have the chance (lack of continuing funds) to complete area (ii).

Technical Approach:

Three graduate students, four postdoctoral fellows, and a visiting scholar have been part of these projects; other postdocs and students were supported through fellowships. We have also initiated a strong theoretical program in ab initio structural and dynamical calculations to compare theory with experiment and new appointments were made for this

purpose. With the efforts of these persons we advanced new methodology for femtosecond-resolved mass spectrometry and for ultrafast electron diffraction. Our plans were in accord with the objective of the original proposal. The following represents the progress made.

Technical Progress:

Our accomplishments have been in three major areas. First, in the area of new techniques we have reported, following the publication in *Nature* of London, on the first clocking of molecular structures using ultrafast electron diffraction, a second publication in *Science* (U.S.A.). We also reported in Chemical Physics Letters on the structures of intermediate carbenes. We have also reported recently the transient structure involved in elimination reactions and more recently we published the structural dynamics of systems far from equilibrium at high energies.

(1) Complex Landscapes of Molecular Structures Imaged by Ultrafast Electron Diffraction: Thermal and Light-Mediated Reactions.
Boyd M. Goodson, Chong-Yu-Ruan, Vladimir A. Lobastov, Ramesh Srinivasan and A. H. Zewail
Chem. Phys. Lett, 374, 417 (2003)

(2) Ultrafast Electron Diffraction of Transient Cyclopentadienyl Radical: A Dynamic Pseudorotary Structure.
H. Ihee, J. S. Feenstra, J. Cao, and A. H. Zewail
Chem. Phys. Lett. 353, 325 (2002)

(3) Ultrafast Electron Diffraction and Structural Dynamics: Transient Intermediates in the Elimination Reaction of C2F412.
H. Ihee, B. M. Goodson, R. Srinivasan, A. Lobastov, nad A. H. Zewail
J. Phys. Chem. A. 106, No. 16, 4087 (2002)

(4) Ultrafast Diffraction of Transient Molecular Structures in Radiationless Transitions.
V. A. Lobastov, R. Srinivasan, B. M. Goodson, C.-Y. Ruan, J. S. Feenstra, and A. H. Zewail
J. Phys. Chem. A, 105, 11159 (2001)

(5) Ultrafast Diffraction and Structural Dynamics - The Nature of Complex Molecules Far From Equilibrium.
C.-Y. Ruan, V. A. Lobastov, R. Srinivasan, B. m. Goodson, H. Ihee and A. H. Zewail
Proc. Natl. Acad. Sci. 98, 7117 (2001)

(6) Direct Imaging of Transient Molecular Structures with Ultrafast Diffraction.
H. Ihee, V. Lobastov, U. Gomez, B. Goodson, R. Srinivasan, C.-Y. Ruan, nad A. H. Zewail
Science 291, 385 (2001)

In the area of reactive intermediates of reactions, we have had success in identifying critical intermediates hitherto unobserved in a variety of reactions. We published on the new finding of nitrogen extrusion reactions, and on the dynamics of diradical intermediates in nonconcerted reactions. We have extended these studies to numerous reactions activated at high energies, including the important class of carbonyl and amine compounds.

(1) Femtosecond of trans-Azomethane: A Combined Experimental and Theoretical Study. Eric W.-G. Diau and A. H. Zewail, ChemPhysChem Submitted for publication.

(2) Coherent Dynamics in Complex Elimination Reactions: Experimental and Theoretical Femtochemistry of 1,3-Dibromopropane and Related Systems.
C. Kotting, Eric W.-G. Diau, T. I. Solling, and A. H. Zewail
J. Phys. Chem. A, 106, 7530 (2002)

(3) Femtochemistry of Norrish Type-I Reactions: III. Highly-Excited Ketones, Theoretical
E. W-G. Diau, C. Kötting, T. I. Sølling, and A. H. Zewail
Chem Phys Chem, 3, 57 (2002)

(4) Femtochemistry of Norrish Type-I Reactions: IV. Highly-Excited Ketones, Experimental
T. I. Sølling, E. W-G. Diau, C. Kötting, S. De Feyter, and A. H. Zewail
Chem Phys Chem, 3, 79 (2002)

(5) Femtochemistry - Atomic-Scale Dynamics of the Chemical Bond
A. H. Zewail
J. Phys. Chem. - Feature Article (Nobel Lecture), 104, 5660 (2000)

(6) Femtosecond Observation of Benzyne Intermediates in a Molecular Beam: Bergman Rearrangement in the Isolated Molecule
E. W.-G. Diau, J. Casanova, J.D. Roberts, and A. H. Zewail
Proc. Natl. Acad. Sci. 97, 1376 (2000)

(7) Femtosecond Dynamics of Retro Diels-Alder Reactions: The Concept of Concertedness
E. W.-G. Diau, S. De Feyter, and A. H. Zewail
Chem. Phys. Lett. 304, 134 (1999)

(8) Direct Observation of the Femtosecond Nonradiative Dynamics of Azulene in a Molecular Beam: The Anomalous Behavior in the Isolated Molecule
E. W.-G. Diau, S. De Feyter, and A. H. Zewail
J. Chem. Phys. 110, 9785 (1999)

(9) Femtosecond ß-Cleavage Dynamics: Observation of the Diradical Intermediate in the Non-concerted Reactions of Cyclic Ethers
A. A. Scala, E. W.-G. Diau, Z. H. Kim, and A. H. Zewail
J. Chem. Phys. 108, 7933 (1998)

(10) Femtosecond Dynamics of Transition States and the Concept of Concertedness: Nitrogen Extrusion of Azomethane Reactions
E. W-G. Diau, O. Abou-Zied, A. A. Scala, and A. H. Zewail
J. Am. Chem. Soc. 120, 3245 (1998)

Finally, in the area of the dynamics of highly energized molecules, we have reported in Science magazine on the non-ergodic behavior of molecules hitherto unobserved in real time, and made extensions to other systems.

(1) Orientation Dynamics and Molecular Structures from Gas Phase to Condensed Media. J. S. Baskin and A. H. Zewail, in: Femtochemistry and Femtobiology: Ultrafast Dynamics in Molecular Science; ed. A. Douhal and J. Santamaria (World Scientific, Singapore, 2002) - Book Chapter

(2) The Uncertainty Paradox - The Fog that was Not
A. H. Zewail
Nature (London) 412, 279 (2001)

(3) CF2XCF2X and CF2XCF2 radicls (X=CL, Br, I): Ab Initio and DFT Studies and Comparisons with Experiments
H. Ihee, J. Kua, W. A. Goddard III, and A. H. Zewail
J. Phys. Chem A 105, 3623 (2001)

(4) Femtosecond Transition State Dynamics of Cis-Stilbene
T. Baumert, T. Frohnmeyer, B. Kiefer, P. Niklaus, M. Strehle, G. Gerber, and A. H. Zewail
Appl. Physics B, Lasers and Optics 72 105 (2001)

(5) Molecular Structure and Orientation: Concepts from Femtosecond Dynamics
J. S. Baskin and A. H. Zewail
J. Phys. Chem. 105, 3680 (2001)

(6) Direct Observation of Resonance Motion in Complex Elimination Reactions: Femtosecond Coherent Dynamics in Reduced Space
C. Kotting, E. W.-G. Diau, J. E. Baldwin, and A. H. Zewail
J. Phys. Chem. A 105, 1677 (2001)

(7) Femtosecond Activation of Reactions and the Concept of Non-Ergodic Molecules
E. W.-G. Diau, J.L. Herek, Z.H. Kim, and A. H. Zewail
Science 279, 847 (1998)

(8) Femtosecond dynamics of hydrogen elimination: benzene formation from cyclohexadiene
S. De Feyter, E. W.-G. Diau, and A. H. Zewail
Phys. Chem. Chem. Phys., Roger Grice Special Issue, 2, 877 (2000)

(9) Femtosecond Dynamics of Norrish type-II Reactions: Non-concerted Hydrogen-Transfer and Diradical Intermediacy
S. De Feyter, E. W.-G. Diau, and A. H. Zewail
Angew. Chem. Int. Ed. Engl. 39/1, 260 (2000)

TECHNOLOGY TRANSFER

Our interaction in the area of Technology Transfer involves two organizations. With the Jet Propulsion Laboratory we have direct scientific interaction on the development of new detectors for the studies of ultrafast electron diffraction. With the Navy Research Laboratories we plan scientific interactions regarding research on molecular explosives and the dynamics of unique substances which store and transfer energy.

ONR DATABASE STATISTICS

- 25 Papers Published in Refereed Journals Citing ONR Support, 3 Papers in Press in Refereed Journals Citing ONR Support.
- 5 Books or Chapters Published Citing ONR Support, 2 Books or Chapters in Press Citing ONR Support.
- 0 Technical Reports & Non-Refereed Papers, 0 Invention Disclosures Citing ONR Support.

- 0 Patents Granted Citing ONR Support, 0 Patents Pending Citing ONR Support
- 23 Presentations, 3 Degrees Granted

Refereed Journal Articles

1. See Technical Section

Books and Chapters

1. See Technical Section

Presentations

1. Commemorative Nobel Prize Symposium Lecture, American chemical Society, Washington D.C. (2000)
2. Honorary Degree Address, Prix Nobel Conference, University of Liege, Belgium (2000)
3. Jubilee Plenary Lecture, Pontifical Academy of Sciences, Vatican City, Rome (2000)
4. Schrodinger Lecture, Imperial College, London, United Kingdom (2000)
5. John C. Polanyi Nobel Laureate lecture, University of Toronto, Canada (2000)
6. DuPont-Marshall Lectureship, University of Pennsylvania, Philadelphia (2000)
7. Schrodinger's Wave Mechanics (75h) Celebration Lecture, University of Zurich, Switzerland (2001)
8. George B. Kistiakowsky Lecture, Harvard University, Cambridge, Massachusetts (2001)
9. National Science Foundation Distinguished Lecture (MPS), Arlington, Virginia (2001)
10. Robbins Lecture Series, Pomona College, Claremont, California (2002)
11. Leon Pape Lecture Series, California State University, Los Angeles (2002)
12. Opening Lecture, Nobel Prize Winner, Lindau, Germany (2002)
13. Linnett Lecture Series, Cambridge University, United Kingdom (2002)

14. California Science Fair, Los Angeles (2002)

15. Frontier in Science, Georgia Tech, Atlanta (2003)

16. Public Lecture, University of Dublin, Trinity College (2004

17. Oxford Honorary Degree Lecture, University of Oxford (2004)