Observing the Femtoworld of Molecules: The 1999 Nobel Prize in Chemistry

George B. Kauffman* **and Laurie M. Kauffman**

Department of Chemistry, California State University, Fresno, Fresno, CA 93740-8034, georgek@csufresno.edu

Abstract: The Egyptian-born chemist Ahmed H. Zewail of the California Institute of Technology, Pasadena was awarded the 1999 Nobel Prize for Chemistry "for his studies of the transition states of chemical reactions using femtosecond spectroscopy." Zewail's career is described from his youth in Egypt to his latest discoveries in the field that he almost single-handedly developed, with extensive quotations from the laureate. The advances in chemical dynamics from the turn of the 20th century to the present are reviewed with emphasis on Zewail's contributions. Applications and future possibilities for femtochemistry are also considered.

Introduction

On December 10, 1999, the 103rd anniversary of Alfred Nobel's death, in Stockholm's *Konserthus* (Concert Hall), Sweden's King Carl XVI Gustav awarded the 1999 Nobel Prize for Chemistry to Professor Ahmed H. Zewail, 53, of the California Institute of Technology, Pasadena (Figure 1). The prize (7,900,000 Swedish kronor, estimated to range from about $939,500 to $1 million) was awarded "for his studies of the transition states of chemical reactions using femtosecond spectroscopy" [1–28] (Figures 2–5). It was the first time since 1994, when George A. Olah won the Nobel chemistry prize [29] that the prize had been awarded to a single individual. Zewail was the first Egyptian-born Nobel laureate in the fields of chemistry, physics, and physiology or medicine. He was also the first University of Pennsylvania Ph.D. graduate to receive the chemistry prize [4].

Zewail's prize marked the 13th time that the Nobel chemistry prize has been awarded for work involving various aspects of chemical dynamics. The 22 recipients in question were: Jacobus Henricus van't Hoff (1901); Svante A. Arrhenius (1903); Wilhelm Ostwald (1909); Georg de Hevesy (1943); Cyril N. Hinshelwood and Nikolai Nikolaievich Semenov (1956); Manfred Eigen, Ronald W. Norrish, and George Porter (1967); Kenichi Fukui and Roald Hoffmann (1981); Henry Taube (1983); Dudley R. Hershbach and Yuan Tseh Lee (1986); Rudolph A Marcus (1992); Paul J. Crutzen, Mario J. Molina, and F. Sherwood Rowland (1995); and Walter Kohn and John A. Pople (1998) [30]. Also, in 1976, his first year at Caltech, he had received a grant from Research Corporation, which makes him the 28th Research Corporation grantee to be awarded the Nobel Prize.

According to the Royal Swedish Academy of Sciences:

> This year's laureate in Chemistry is being rewarded for his pioneering investigation of fundamental chemical reactions, using ultra-short laser flashes, on the time scale on which reactions actually occur. Professor Zewail's contributions have brought about a revolution in chemistry and adjacent sciences, since this type of investigation allows us to understand and predict important reactions [1].

Tuesday, October 12, 1999, brought both good news and bad news to Zewail (Figure 6). The good news: He was awakened in his San Marino, California home at 5:40 a.m. by a phone call from the Royal Swedish Academy of Sciences, informing him of the award and warning him that "These are the last 20 minutes of peace in your life" [6, 22]. The bad news: He had awakened with a cold, a minor annoyance that he quickly forgot in the ensuing 2000 or so e-mails of congratulations from friends and colleagues. Three phone lines began to ring with requests for interviews from the U.S., Egyptian, and other foreign presses. The correspondence exceeded 5,000 messages by mid-November.

After kissing his wife, Dema, and sons, Nabeel and Hani, ages 6 and 5, respectively (Figure 7), Zewail telephoned his mother in Egypt, who cried with joy and excitement at the news. When he called his daughters Maha, a Caltech alumna, and Amani, a University of California, Berkeley chemistry student, he was so overcome that he couldn't speak. His older son, Nabeel, accepted the great news with typical juvenile aplomb. When Zewail asked him if he would tell his classmates, the six-year-old replied, "No. These guys will say, 'So what?'" However, Nabeel did ask, "Are we going to see the King?" [22].

Youth in Egypt

Ahmed Hassan Zewail was born on February 26, 1946 in Damanhur, the city of Horus, the Egyptian falcon god, about 40 miles southeast of Alexandria, the home of ancient learning and site of the world-famed library of antiquity [2, 31–33]. Founded by Alexander the Great at the mouth of the Nile in 331 B.C., Alexandria is generally considered the site of the origin of chemistry and of the activity of the Hellenistic alchemists, who were among the forerunners of today's chemists [34]. The word "chemistry" first occurs in an edict of the Roman emperor Diocletian in A.D. 296 ordering that Alexandrian books on *chemeia*, the art or science of making (imitating) gold and silver, be burnt. The word appears in the Greek authors who report this as *χημεια*. It is not Greek but is derived from the designation for Egypt, a country that the Greek author Plutarch in his treatise *On Isis and Osiris* (ca. A.D. 100) states is called *chemia* because of the black color of

---

[*] Series Editor contribution.

© 2002 Springer-Verlag New York, Inc., S1430-4171(02)02534-6, Published on Web 03/15/2002, 10.1007/s00897020534a, 720100gk.pdf

Figure 1. Ahmed H. Zewail. Reference 6, p 6. (Courtesy, California Institute of Technology.)

Figure 2. The 1999 Nobel Prize Ceremony, December 10, 1999. (Courtesy, the Nobel Foundation.)

Figure 3. King Carl XVI Gustav of Sweden (right) presents the 1999 Nobel Prize in Chemistry to Ahmed H. Zewail (left). (Courtesy, the Nobel Foundation.)

Figure 4. The 1999 Nobel Prize in Chemistry Medal. (Courtesy, the Nobel Foundation.)

Kungliga
Svenska Vetenskapsakademien
har den 12 oktober 1999 beslutat
att med det
NOBELPRIS
som detta år tillerkännes den
som gjort den viktigaste kemiska
upptäckten eller förbättringen
belöna
Ahmed H Zewail
för hans studier av
kemiska reaktioners övergångstillstånd
med femtosekundspektroskopi

Figure 5. The 1999 Nobel Prize in Chemistry Diploma. Artist, Nils G. Stenqvist; Calligrapher, Annika Rücker. http://www.nobel.se/chemistry/laureates/1999/zewail-diploma.html. (Courtesy, the Nobel Foundation.)

Figure 6. Ahmed H. Zewail (waving) flanked by his wife Dema; Caltech President David Baltimore (far left); and colleagues on the Pasadena campus, where he met the press, following the announcement that he had won the Nobel Prize. Reference 9, p 12. Photograph by Robert J. Paz. (Courtesy, California Institute of Technology.)

Figure 7. Going to see the King. Ahmed H. Zewail with his wife, Dema, and sons, Hani (left) and Nabeel. Reference 22, p 11. (Courtesy, California Institute of Technology.)

its soil, enriched by the seasonal overflowing of the Nile [34]. Thus Zewail's choice of chemistry as a career is not surprising.

The only son of Hassan A. Zewail and his wife Rawhia (née Dar), young Ahmed spent a happy childhood with his parents and three sisters in Disuq. The town is located on the banks of the Rosetta branch of the Nile, about 20 miles northwest of his birthplace and the site of the Sidi Ibrahim mosque. A mere 20 miles to the northeast was the city of Rosetta (Rashid), where the stone bearing an inscription in hieroglyphics, demotic, and Greek that furnished the crucial key to the decipherment of ancient Egyptian texts was discovered in 1799. Similarly, Ahmed was to provide the key to interpreting the actual course of chemical reactions.

Ahmed's father, a cheerful man liked and respected in the community, was a government employee. In his spare time he was an owner of a motorcycle and bicycle business. His mother, a good-natured, contented person, was devoted to her children, especially her precocious son, and exerted a central influence on his life.

Education was an important *desideratum* in the Zewail family. The family's dream was for Ahmed to receive an advanced degree abroad and to return to his homeland as a university professor. During his youth, they placed a sign reading "Dr. Ahmed" on his study room door. His favorite uncle, Rizk Dar, who was financially well-off, self-educated, and respected for his wisdom, taught him to appreciate critical analysis, music, and the intermingling of both the masses and intellectuals. Ahmed's youthful interests included reading (still a major avocation), music (especially the songs—*waslats*—of the female superstar Um Kulthum; in America he favors classical and jazz), some sports, and backgammon.

Young Ahmed gravitated early to the physical sciences, mathematics, mechanics, and chemistry, but he eschewed the social sciences because of the extensive memorization then involved. Although his inquiring mind always asked "How?" and "Why?," a trait that has persisted to this day, and chemistry did require some memorization, he was intrigued by the "mathematics of chemistry." Furthermore, it provided laboratory phenomena that he enjoyed reproducing and understanding. In his bedroom he constructed a distillation apparatus from his mother's oil burner for making Arabic coffee so that he could observe the transformation of wood into a burning gas and a liquid.

After graduating from high school, Zewail applied to the central bureau (*Maktab El Tansiq*) that assigns candidates to a university based on their grades. His lifelong passion for science was fulfilled, for he was admitted to the Faculty of Science of Alexandria University, where he excelled in mathematics, physics, chemistry, and geology. During his sophomore year he scored "excellent" in chemistry and was chosen as part of an elite group of seven students (called "Special Chemistry"). Because of his excellent grades, while still a student, he was awarded a monthly stipend, the amount of which was almost that of a university graduate. During 1966 he was a Shell Corporation Undergraduate Trainee.

In 1967 Zewail received his B.S. degree ("Distinction with First Class Honors," above 90 percent in all areas of chemistry). He was then appointed to a tenured position as a Demonstrator (*Moeid*) to teach undergraduates and to pursue graduate studies (Figure 8). Although not a professor, he was so successful in his teaching that he gave "professorial lectures" to help students after the professor had given his lecture. In Zewail's own words,

> Through this experience I discovered an affinity and enjoyment of explaining science and natural phenomena in the clearest and simplest way….I believed that behind every universal phenomenon there must be beauty and simplicity in its description [2].

Zewail finished the requirements for his M.S. degree in about eight months (1968). His research under advisors Professors Tahany Salem, Rafaat Issa, and Samir El-Ezaby involved the change of spectra of molecules in different solvents and resulted in several publications [35]. Professors El-Ezaby and Yehia El Tantawy, graduates of the Universities of Utah and Pennsylvania, respectively, encouraged Zewail to complete his doctoral research abroad in the United States. The odds were against his doing so (He had no contacts abroad, and because the 1967 Middle East war had just ended, study missions were being sent only to the USSR or Eastern European countries); therefore, he had to obtain a scholarship directly from an American university. After corresponding with a dozen universities, he received offers from several of them, and he decided to accept a scholarship paying tuition plus a monthly stipend from the University of Pennsylvania in Philadelphia.

Stranger in a Strange Land

After surmounting frustrating regulatory and bureaucratic barriers, Zewail departed from Egypt. According to his recollections of the early stages of this *Exodus*,

> Arriving in the States, I had the feeling of being thrown into an ocean. The ocean was full of knowledge, culture, and opportunities, and the choice was clear: I could either learn to swim or sink. The culture was foreign, the language was difficult, but my hopes were high. I did not speak or write English fluently, and I did not know much about western culture in general, or American culture in particular [2].

As *the* Egyptian at Penn, Zewail made his presence felt on campus among faculty and students alike by his high grades, his talent for teaching (Teaching Assistant, 1969–70; Predoctoral Research Fellow, 1970–74), and successful research under the supervision of Robin M. Hochstrasser (b. 1931), now Donner Professor of Physical Sciences (Figure 9). Hochstrasser recalls,

> When he first came into my office, having just arrived from Egypt, he had to use his wife as an interpreter in our discussions. However, he learned English and quantum mechanics very quickly, did some first rate experiments here and wrote an outstanding Ph.D. thesis. He was among my most promising students at the time [12]. He was a very good student. He was always seeking research avenues that would take him into new territory. He did this as a student and continued with the same approach later. It was clear from the beginning that he had the potential for an outstanding research career. His femtosecond (1 fs = 10^{-15} s, from Danish-Norwegian *femten*, "fifteen" [36]) laser experiments on the synchronous excitation of small molecules have had a tremendous impact on chemistry and on the way in which chemists picture a molecule in the process of undergoing a chemical reaction [4].

Among his courses Zewail particularly enjoyed those in physics taught by 1972 Nobel physics laureate John R. Schrieffer. As he expressed it,

> The diverse research problems I worked on, and the collaborations with many able scientists were both enjoyable and profitable. My publication list was increasing, but just as importantly, I was learning new things literally every day—in chemistry, in physics, and in other fields. The atmosphere at the Laboratory for Research on the Structure of Matter was most stimulating, and I was enthusiastic about researching in areas that crossed the disciplines of physics and chemistry (sometimes too enthusiastic!)….I was working almost "day and night" and doing several projects at the same time: the

Figure 8. Ahmed H. Zewail (third from left) with fellow students at the University of Alexandria, 1966. (Courtesy of Ahmed H. Zewail, biographical collection.)

Figure 9. A meeting of minds. (From left to right) Robin M. Hochstrasser, Kenneth B. Eisenthal, Charles B. Harris, Ahmed H. Zewail, and Shaul Mukamel, late 1970s. (Courtesy of Ahmed H. Zewail, biographical collection.)

> Stark effect of simple molecules [37]; the Zeeman effect of molecular solids like NO_2^- and benzene [38]; the optical detection of magnetic resonance (ODMR) [39]; double resonance techniques, etc. Now, thinking about it, I cannot imagine doing all of this again, but, of course, then I was "young and innocent" [2].

By 1973 Zewail had essentially completed all the requirements for his doctorate, including his research on the spectroscopy of dimers, but that year another war erupted in the Middle East, which resurrected strong feelings in him about his original plan of returning to Egypt to become a university professor. However, he realized that his homeland would not be able to provide the scientific atmosphere that he had enjoyed in the United States. Furthermore, several years in America would give him and his family two opportunities. He could enrich his experience by entering another research area in another university, and with a salary higher than that of a graduate student he "could then buy a big American car that would be so impressive for the new professor at Alexandria University!" [2]. He therefore applied for postdoctoral fellowships at five universities—three in the United States, one in Germany, and one in the Netherlands. Of the five offers that he received he chose the one at the University of California, Berkeley.

After receiving his Ph.D. degree from Penn in 1974 (Figure 10), Zewail and his family moved from Philadelphia to Berkeley, a change that he described as "culturally…almost as much of a shock as the transition from Alexandria to Philadelphia" [2]. Yet, "the obstacles did not seem as high as they had when [he] came to the University of Pennsylvania because culturally and scientifically [he] was better equipped" [2]. He worked with Professor Charles B. Harris (b. 1940), who offered him a prestigious IBM Postdoctoral Fellowship (1974–76). Using the expertise gained in his doctoral research and the new tools available to him in Berkeley, he measured the coherence of dimers [40], a theoretical and experimental knowledge of which proved vital in his subsequent research. In his first independently authored articles [41] he extended the concept of coherence to multidimensional systems, and in collaboration with other graduate students he authored articles on energy transfer in solids [42].

Harris persuaded Zewail to seek a position at one of the top American universities or at least to gain the experience of being interviewed for such a position. Zewail applied to several universities, contacted Egypt, and considered the American University in Beirut. Although he visited several campuses, no offer materialized, and he was preparing for his return to Alexandria. Meanwhile, he and Harris began to build a picosecond (1 ps = 10^{-12} s, from the Spanish *pico*, "a bit," or Italian *piccolo*, "small" [36]) laser, and he learned a great deal about the principles and physics of lasers.

When many of the best universities announced the availability of new faculty positions, he applied to almost a dozen places and was offered assistant professorships at many of them, including the California Institute of Technology, the University of Chicago, and Harvard, Northwestern, and Rice Universities. He joined the faculty of Caltech at Pasadena, where he has served as Assistant Professor of chemical physics (1976–78), Associate Professor with tenure (1978–82), Professor (1982–89), and the first Linus Pauling Professor (1990–94, Figure 11). He takes particular pride in being at the same institution where Pauling, his scientific hero and role model, carried out his own Nobel Prize–winning work on the nature of the chemical bond (Figure 12). Coincidentally, both men were the same age (53), almost to the day, when they won the prize—Pauling for static, stable, and enduring bonds and Zewail for dynamic and alive bonds [6]. According to Caltech President David Baltimore (b. 1938), himself a Nobel laureate (Physiology or Medicine, 1975), "It's not just another prize. You have to see Ahmed as the inheritor of the tradition that Linus Pauling started by seeing chemistry as a molecular process" [18].

Since 1995 Zewail has been Linus Pauling Professor of Chemical Physics and Professor of Physics and, since 1996, Director of Caltech's National Science Foundation Laboratory for Molecular Sciences (LMS). Through the years, the members of his research group, to whom he is known affectionately as "A. Z.," have been what he calls a "village of science." They have included almost 150 graduate students, postdoctoral fellows, and visiting associates with diverse backgrounds, cultures, and abilities. They came from various countries all over the world, and many of them now occupy leading academic, industrial, and governmental positions (Figures 13 and 14). He considers "working with such minds in a *village of science* the most rewarding experience" of his life [2].

In view of the endless hours that Zewail's students and postdocs spend in the laboratory, some persons on the Caltech campus view him as a "slave driver," but one of his graduate students, Hyotcherl Ihee, disagreed, "That's not true. We are inspired by his passion for science" [18]. Researcher Boyd Goodson expressed admiration at Zewail's patient and upbeat nature: "Even if the experiment doesn't work, he's still excited and finds something that's good about it" [18]. Concerning the Nobel Prize, postdoc Mirianas Chachisvilis, who joined

Figure 10. Ahmed H. Zewail. Ph.D. graduation photograph, 1974. (Courtesy of Ahmed H. Zewail, biographical collection.)

Figure 11. Professor Linus Pauling (left) and the Linus Pauling Professor (Ahmed H. Zewail, right). Reference 6, p 17. (Courtesy of Ahmed H. Zewail, biographical collection.)

Figure 12. Faculty of Caltech Chemistry and Chemical Engineering Departments at Linus Pauling 85th Birthday Celebration organized by Ahmed H. Zewail, 1986. Zewail (first row, extreme left); Pauling (first row, sixth from left). (Courtesy of Ahmed H. Zewail, biographical collection.)

Figure 13. Ahmed H. Zewail's research group on the day of the Nobel Prize announcement, October 12, 1999. (Zewail, eighth from left). (Courtesy of Ahmed H. Zewail, biographical collection.)

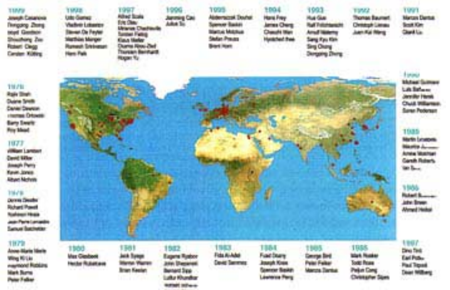

Figure 14. The international roster of Zewail's Caltech research group (1976–1999). The red circles are usually composites of many dots, reflecting the more than one hundred graduate students, postdoctoral fellows, and visiting associates who made up the research team over the years. Reference 2, p 194. (Courtesy, the Nobel Foundation.)

Figure 15. The Zewail family. Amani, Hani, Ahmed, Nabeel, Dema, and Maha (from left to right), 1996. (Courtesy of Ahmed H. Zewail, biographical collection.)

Zewail's group of 15 researchers in 1992, stated, "It was overdue. It was clear to me that he would get it one day" [18]. At a news conference in Pasadena after the Nobel announcement, Zewail protested that he was just a "regular guy": "I like to go to the cinema. I like Greek restaurants, and I like to spend time with my wife and kids. I'm just the same as everyone else" [17].

Despite his enthusiasm for almost everything American, Zewail is critical of the lack of attention that the media give to science:

> We live in one of the most advanced nations on Earth in science and technology, and we don't have one hour a week devoted to science on national network television [43].

All of Zewail's four children were born in the United States. His two daughters from his first marriage are Maha, 28, a Caltech alumna and Ph.D. student in medicinal chemistry at the University of Texas, Austin and Amani**,** 21, a junior chemistry student at the University of California, Berkeley (Figure 15). He met his present wife, Dema (née Faham), a Syrian physician, in a chance encounter of March 1989 that he characterized as "a fairy tale." They were in Riyadh, Saudi Arabia, where Zewail was receiving the King Faisal International Prize in Science "for pioneering and excellent work on ultrafast laser chemistry" [44], and Dema's father, Chaker Faham, was receiving the same prize in literature. The couple became engaged in July 1989 and married in September. Dema received her M.D. degree from Damascus University and her Master's degree from the University of California, Los Angeles. Ahmed's friend and confidante, she is a wonderful mother to their two sons, Nabeel and Hani.

One of the problems of Zewail's homeland has been the economic disaster resulting from the "brain drain" of intellectuals, who emigrated to the United States, Europe, and

Australia. The exodus is said to have begun following Egypt's war with Israel in 1967 and the disappointment with the outcome of that war [44]. But Zewail's recent Nobel Prize has highlighted the position of Egyptians and those with dual nationalities, and Egyptian media have begun to call for improved relations between Egypt and its "emigrant birds abroad" [44]. In 1993, in order to reverse the decades-long brain drain and to create a homegrown biotechnology industry, President Mubarak issued a decree to create the Mubarak City for Scientific Research and Technological Applications (MUCSAT) in the desert about 13 miles south of Alexandria. MUCSAT opened in August 2000. Half of its 160 scientists have worked abroad and have chosen to return to their homeland. According to Minister of Higher Education and Scientific Research, Moufid Shehab, "MUCSAT will propel Egypt into the world of advanced technology" [45].

Zewail has never forgotten his roots. Although he became a naturalized American citizen in 1982, he has retained his Egyptian citizenship (Figure 16). He modestly concluded his biographical sketch for the Nobel Prize as follows:

> The journey from Egypt to America has been full of surprises. As a *Moeid*, I was unaware of the Nobel Prize in the way I now see its impact in the West. We used to gather around the TV or read in the newspaper about the recognition of famous Egyptian scientists and writers by the President, and these moments gave my friends and me a real thrill—maybe one day we would be in this position ourselves for achievements in science or literature. Some decades later, when President [Muhammad Hosni] Mubarak bestowed on me [in 1995] the Order of Merit, first class [Science & Arts] and [in 1999] the Grand Collar of the Nile (*Kiladate El Nile*), the highest State honor (Figures 17 and 18), it brought these emotional boyhood days back to my memory. I never expected that my portrait, next to the pyramids (Figures 19 and 20), would be on a [December 10,] 1999 postage stamp or that the school I went to as a boy, Desuq High School, and the road to Rosetta would be named after me. Certainly, I never dreamed that one day I would be honored with the Nobel Prize [2].

Major Activities

The author or editor of eight books [46–53] and almost 400 articles, in 1989 Zewail was elected to the National Academy of Sciences at the early age of 43 (Most members are usually in their mid-50s or older when they are chosen for this prestigious honor). He was also elected to more than ten other academies and societies, including the prestigious Pontifical Academy of Sciences [54] and the Royal Society of London. He holds a patent in the solar energy field [55]. He has presented more than 400 invited lectures (150 of them named and plenary lectures) and has been a visiting professor at a baker's dozen of universities in the United States, Belgium, England, Egypt, France, Germany, Kuwait, and the Netherlands. He has been in demand as an advisor and has been the chairman or member of numerous organizing committees of many international conferences. He is among the Institute for Scientific Information's (ISI's) "50 Most Cited Chemists for the period 1981-June 1997."

Zewail has served as Editor and has been a member of the editorial and advisory boards of several scientific journals, including *Laser Chemistry* (1980–85), *Journal of Physical Chemistry* (1985–90), and *Chemical Physics Letters* (since 1991) as well as of several book series. His work has involved nonlinear laser spectroscopy, radiationless processes in molecules, energy transfer in solids, picosecond spectroscopy, solar photovoltaic conversion, and laser-induced chemistry. His current research is devoted to developments in ultrafast lasers and electrons for studies of dynamics of complex systems with atomic-scale resolution in chemistry and biology. In the field of femtochemistry, developed by him and his group, the focus is on fundamental femtosecond (10^{-15} s) processes in chemistry, physics, and biology. Other areas of major interest include time-resolved structures with ultrafast electron diffraction and the dynamics of biological functions [31].

Honors and Awards

In addition to the awards already mentioned, Zewail's honors include the following [2, 31–33, 56–58]; the Alfred P. Sloan Foundation Fellowship (1978–82); Camille and Henry Dreyfus Teacher-Scholar Award (1979–85); Alexander von Humboldt Award for Senior U.S. Scientists (1983); National Science Foundation Award for especially creative research (1984, 1988, 1993); John Simon Guggenheim Memorial Foundation Fellowship (1987); NASA Award (1991); Carl Zeiss International Award, Germany (1992); Medal of the Royal Netherlands Academy of Arts & Sciences; Earl K. Plyer Prize, American Physical Society; Wolf Prize in Chemistry (1993); Bonner Chemiepreis, Germany (1994); Leonardo da Vinci Award of Excellence, France; Collège de France Medal; Herbert P. Broida Prize, American Physical Society (1995); National Academy of Sciences Award, Chemical Sciences; John G. Kirkwood Medal, Yale University; Peking University Medal, Beijing, China (1996); Pittsburgh Spectroscopy Award; Linus Pauling Medal; Robert A Welch Award in Chemistry (1997); Richard C. Tolman Medal; Benjamin Franklin Medal, Franklin Institute; Paul Karrer Gold Medal, Universität Zürich, Switzerland; Ernest O. Lawrence Award, U.S. Government (1998); Merski Award, University of Nebraska; and Röntgen Prize (100th anniversary of the discovery of X-rays), Germany (1999). On May 14, 2001 he was elected a foreign member of the Royal Society, London.

Zewail holds honorary degrees from Oxford University (M.A., 1991); American University, Cairo, Egypt (D.Sc., 1993); Katholieke Universiteit, Leuven, Belgium (Figure 21); University of Pennsylvania (Figure 22); and Université de Lausanne, Switzerland (all D.Sc.; all 1997); Swinburne University, Australia (D.U., 1999); Arab Academy for Science & Technology, Egypt (H.D.A.Sc., 1999); Alexandria University, Egyptian (H.D.Sc., 1999); University of New Brunswick, Canada (D.Sc., 2000); Université de Liège, Belgium (D., 2000).

Zewail's American Chemical Society awards include the Buck–Whitney Medal (1985), Harrison Howe Award (1989), Peter Debye Award in Physical Chemistry (1996, a year before his mentor Robin M. Hochstrasser), Nobel Laureate Signature Award for Graduate Education in Chemistry (1992, with student Marcos Dantus, now at Michigan State University [56]), E. Bright Wilson Award in Spectroscopy (1997, the first recipient of this award), and William H. Nichols Medal (1998) [56].

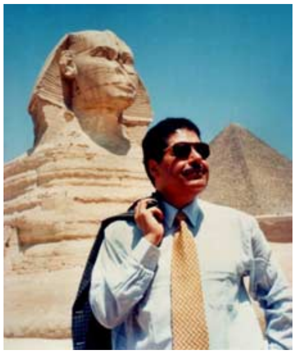

Figure 16. Ahmed H. Zewail with sphinx and pyramid, 1998. (Courtesy, the Nobel Foundation.)

Figure 17. Awarding of the Grand Collar of the Nile, 1999. Ahmed H. Zewail (left) and Egyptian President Hosni Mubarak (applauding, right). (Courtesy of Ahmed H. Zewail, biographical collection.)

Figure 18. The Grand Collar of the Nile (*Kiladate El Nile*), 1999. (Courtesy of Ahmed H. Zewail, biographical collection.)

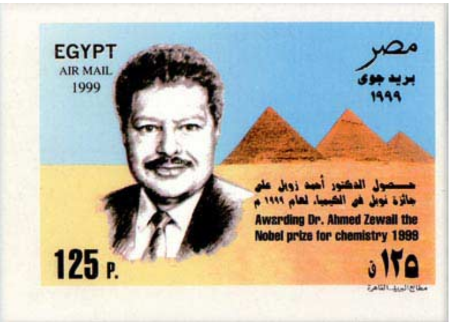

Figure 19. “Awarding Dr. Ahmed Zewail the Nobel Prize for Chemistry 1999.” Egyptian air-mail postage stamp, issued December 10, 1999 (Scott Catalogue No. 1729, 125 piasters, imperforate). (Courtesy of Ahmed H. Zewail, biographical collection.)

Figure 20. George B. Kauffman (left) and Laurie M. Kauffman (right) wearing T-shirts bearing an earlier Egyptian postage stamp, issued June 14, 1998 when Zewail was awarded the Franklin Institute award (Scott Catalogue No. 1685, 20 piasters). The issue also included a yellow, green, and black £1 air mail stamp (Scott Catalogue No. 1686). Photograph by Randy Vaughn-Dotta. (Courtesy, Randy Vaughn-Dotta.)

Figure 21. Ahmed H. Zewail (left) and H. M. King Albert II of Belgium (right) after presentation of honorary D.Sc. degree from Katholieke Universiteit, Leuven, 1997. (Courtesy of Ahmed H. Zewail, biographical collection.)

Figure 22. Honorary Doctorate Awardees, University of Pennsylvania, 1997. The metallic gentleman sitting on the bench is Benjamin Franklin (1706–1790), who founded the University of Pennsylvania in 1740. Ahmed H. Zewail is standing, second from right. (Courtesy of Ahmed H. Zewail, biographical collection.)

The Measurement of Time

In the history of civilization the measurement and recording of the order and duration of time, one of science’s two fundamental dimensions, the other being space, are among man’s earliest scientific activities [2, 3, 60]. At the dawn of

© 2002 Springer-Verlag New York, Inc., S1430-4171(02)02534-6, Published on Web 03/15/2002, 10.1007/s00897020534a, 720100gk.pdf

written language Zewail's ancestors developed calendars to track the yearly flooding of the Nile valley in ancient Egypt, and the ancient Mesopotamians devised calendars for following the seasons for planting and harvesting. By 1500 B.C. sun clocks were used in Egypt to time daily and seasonal events. Over millennia humankind has tried to explore events on an ever-shorter time scale. However, until the 19th century the ability to time events was limited to scales amenable to direct sensory perception, for example, no faster than the blink of an eye (ca. 0.1 second) or the ear's recognition of a tone (e.g., 0.1 millisecond) (Figure 23).

In 1872 millionaire California ex-governor Amasa Leland Stanford (1821–1893), founder and endower of Stanford University, wagered $25,000 with a millionaire friend that at times all four of a galloping horse's hooves were off the ground [6, 60–62]. He employed eccentric English photographer Eadweard Muybridge (1830–1904) to decide the matter. Muybridge allowed a horse to run at a speed of about 10 meters per second (32 ft/s) past a row of a dozen cameras with exposure times of about 0.001 second. He proved Stanford's assumption correct with a series of photographs reproduced as an engraving on the cover of the October 19, 1878 issue of *Scientific American* (Figure 24). Since that time more and more sophisticated developments in high-speed photography have been used to revolutionize our understanding of motions that are faster than the eye can follow in scientific disciplines from aeronautics to zoology (Figure 25).

Scientists have long hoped for a technique that would enable them to capture the actual high-speed motion of molecules much as slow-motion replays capture the high-speed action of televised sports events. Whereas movements of athletes occur on the order of hundredths of a second, atoms and molecules react so rapidly that they occur on a time scale of several quadrillionths of a second (one femtosecond or fs = 10^{-15} s). Thus a shutter speed 100 billion times as fast as Muybridge's camera would be required to "photograph" their motion. A femtosecond is a fantastically small unit of time; 1 fs is to a second as a second is to 32 million years [6]. In one second light travels from the earth to the moon, while in one femtosecond it travels a fraction of a human hair's breadth. Chemistry Professor A. Welford Castleman, Jr. of Pennsylvania State University uses the following analogy for his students: If all the sand particles in 25 football fields, each filled with sand to a depth of three feet, are equal to one second, then a single sand particle in all those fields would equal one femtosecond [62].

What was to become known as femtochemistry became possible because of both theoretical and technical developments.

Developments in Theory: From Kinetics to Dynamics

A century before Zewail was awarded the Nobel Prize, Svante August Arrhenius (1859–1927), who was to receive the 1903 Nobel Prize for Chemistry for his theory of electrolytic dissociation, proposed the equation that bears his name relating the change in rates of chemical reactions with temperature [63]:

$$R = Ae^{-Ea/kT}$$

where R is the reaction rate, A is the frequency factor, E_a is the activation energy, k is the rate constant, and T is the absolute temperature (Figure 26).

This equation, as Arrhenius himself admitted, had its roots in the 1884 equations [64] of Jacobus Henricus van't Hoff (1852–1911), the first Nobel chemistry laureate. However, Arrhenius' rate constant, k, was derived from a *macroscopic* average of the *microscopic* rate coefficients for all possible molecular encounters and did not provide a detailed molecular picture for the reaction. What was lacking was a method to describe quantitatively the process of the reaction itself, that is, how reactant molecules approach, collide, exchange energy, break old bonds and form new ones, and separate into products [3]—the goals of molecular reaction dynamics [65].

It was not until the 1930s that Henry Eyring (1901–1981) [66] and Michael Polanyi (1891–1976) predicted that reactions should occur at femtosecond time scales. They formulated a semiempirical calculation of a potential energy surface (PES) of the $H + H_2$ reaction that described the path of nuclei from the reactants to the products, passing through the transition state of activated complexes [67]. This birth of reaction dynamics allowed chemists to think of the PES and the trajectories of dynamics, often expressed in atomic units of time [68]. However, inasmuch as the time scale for the activated complexes of the transition state was estimated to be less than one picosecond (10^{-12} s), at the time there was little hope of observing the transient molecular structures of a chemical reaction.

Developments in Technology: Molecular Beams and Lasers

Around mid-century Ronald G. W. Norrish (1897–1978) [69] and George Porter (b. 1920) [70] at Cambridge University and Manfred Eigen (b. 1927) [71] at the Max Planck Institute for Physical Chemistry at Göttingen developed techniques for studying reaction intermediates with lifetimes between a thousandth and a millionth of a second (10^{-3} to 10^{-6} s). The trio shared the 1967 Nobel Prize for Chemistry for this work. Porter and Norrish's method of flash photolysis, which employed electronics developed after World War II, produced an intense burst of light and produced free radicals in the sample. Recording the spectra of these radicals by using other light, they observed some relatively stable intermediates and thus studied kinetics on a microsecond (10^{-6} s, from the Latin *micro-* (Greek, μικρος) "small" [36]) scale. By means of his "relaxation method" Eigen was able to reach the microsecond and close to the nanosecond (10^{-9} s, from the Latin *nanus* (Greek, νανος), "dwarf" [36]) scale.

During the 1960s Dudley R. Hershbach (b. 1932) [72] and Yuan T. Lee (b. 1936) [73] used molecular beam techniques, which were also an indispensable part of Zewail's femtochemical investigations, to study chemical reactions during the collision of molecules. The two shared the 1986 Nobel Prize for Chemistry with John C. Polanyi (b. 1929), Michael Polanyi's son [74], for his work on infrared chemiluminescence, which also provided a new approach for studying the dynamics of single collisions using the reaction products. Crossed molecular beam–laser investigations by many scientists such as Richard N. Zare, Richard B. Bernstein, and others [75] have probed dynamics by meticulous analyses of product internal energy distributions and steady-state alignment and orientation of products. However, all these

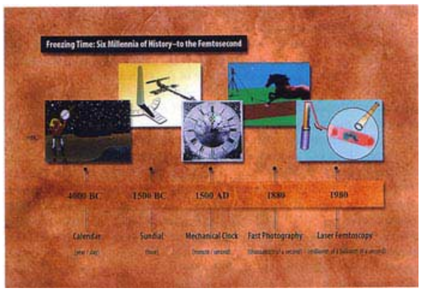

Figure 23. Timeline of some events in the history of units of time, from yearly calendars to the femtosecond regime. Reference 2, p 114. (Courtesy, the Nobel Foundation.)

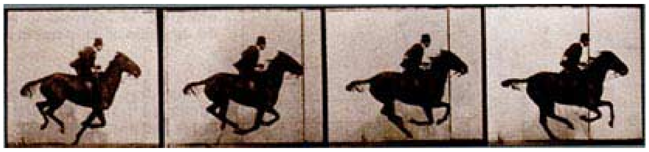

Figure 24. In 1878 photographer Eadweard Muybridge was able to capture movement with the fastest camera of the time. (Courtesy, the Nobel Foundation.)

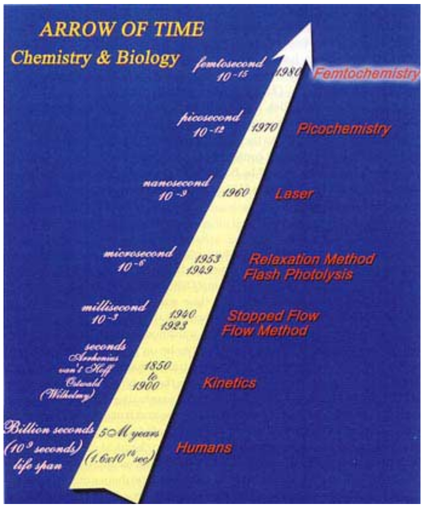

Figure 25. The arrow of time in chemistry and biology, some steps over a century of development. Reference 2, p 126. (Courtesy, the Nobel Foundation.)

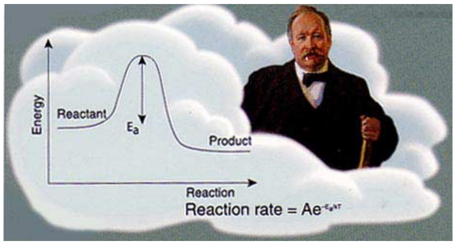

Figure 26. Svante Arrhenius and his equation showing how the rate of a chemical reaction varies with temperature. He related the rate to the height of the energy barrier (E_a) and to the temperature (T). (Courtesy, the Nobel Foundation.)

techniques still could not capture in real time the configurations of the very short-lived intermediate transition states in which bonds stretch or contract during reactions.

In 1960 Theodore H. Maiman (b. 1927) constructed the first laser, a device that produces monochromatic coherent light, that is, light in which the rays are all of the same wavelength and phase. Scientists and technologists then began a race to build lasers that were able to generate ultrashort pulses—nanoseconds (10^{-9} s) and later picoseconds (10^{-12} s) in duration. By the early 1980s Charles V. Shank and co-workers at the AT & T Bell Laboratories produced lasers capable of producing femtosecond (10^{-15} s) pulses. The stage was now set for Zewail and the birth of his brainchild—the field of femtochemistry. New concepts and techniques were then developed to capture the motion of atoms in reactions.

Zewail's Early Years of Coherence

When Zewail arrived at Caltech in 1976, he recalls,

> I was not thinking or dreaming of femtosecond time resolution. But I had the idea of exploring *coherence* as a new concept in dynamics, intra- and inter-molecular. This proved to be vital and fruitful….I made the decision not to begin with the type of picosecond research I was doing at Berkeley as a postdoctoral fellow [40]. Instead, the initial effort was focused on two directions: (i) studies of coherence in disordered solids, and (ii) the development of a new laser program for the study of the phenomenon of (optical) coherence….My experience with Professor Charles Harris was to culminate in these experiments [2].

When Muybridge took his famous stop-motion photographs of a galloping horse in 1887, only one horse was ridden past a row of a dozen cameras [6]. However, in a chemical reaction millions or billions of molecules are reacting—as if Muybridge had run an entire herd of animals in lock step past one camera. Furthermore, in a reaction the molecules do not move in lock step with synchronized gaits.

For his assistant professorship at Caltech Zewail proposed to apply the concept of coherence to his laser research, which was "pretty hot stuff back then" [6]. He carried out his first experiments at Pasadena with graduate students Thomas Orlowski and Daniel Dawson and undergraduate student Kevin Jones. They demonstrated that short laser pulses (then measured in nanoseconds) were able to excite simple or even complex molecules into coherent states and that such coherence could be detected during their spontaneous decay [76–78]. Although each individual molecule in a sample was following its own course, there were some spectroscopic phenomena in which a large percentage of them acted in unison. If shot with a sufficiently brief laser pulse, they would then release the excess energy in a coordinated manner. This discovery brought Zewail his own ultrafast reaction—tenure in less than two years.

Zewail continued research on four areas: optical coherence phenomena and dephasing, disorder in solids, picosecond spectroscopy, and luminescent solar concentrators, the last of which resulted in a patent [55] and several publications. Ironically, the first of these areas did not win immediate acceptance among chemists. According to Zewail,

> In my own department, some colleagues were not too excited about "this stuff of coherence and dephasing"—thinking that it was *not relevant to chemistry!* Many chemists on the outside were also unsure what this was all about. In fact, a notable chemist once said publicly at a conference I attended that coherence and dephasing had nothing to do with chemistry! On the physics side, I was invited to numerous conferences, including one in which the [1955] Nobel Laureate Willis Lamb asked me to have

© 2002 Springer-Verlag New York, Inc., S1430-4171(02)02534-6, Published on Web 03/15/2002, 10.1007/s00897020534a, 720100gk.pdf

> dinner to discuss our research. This was a special experience!
>
> I was not convinced by these doubts and my faith helped us to continue along with the development. The concept of coherence turned out to be fundamental in femtochemistry, and it is now well accepted that coherence is a key process in the probing and controlling of molecular dynamics [2].

Molecular Beams

Zewail then became interested in investigating, not perturbations *between* molecules, which he had just done, but the coherence occurring *within* complex molecules [6]. He isolated these molecules by means of molecular beams, the first of which he built in 1979. He confesses that he knew nothing about this technology but relied on the work of students William R. Lambert and Peter M. Felker, who started "from scratch" [6]. Although molecular beam technology is now quite standard, at that time attempting to combine a molecular beam and an ultrafast laser into a workable apparatus posed tremendous technical problems. Fortunately, Zewail's group had a close relationship with Spectra Physics, the leading manufacturer of high-speed lasers, which provided them with equipment in the early stages of development and production at a substantial discount. According to Lambert, "This enabled us to perform experiments everyone in the field wanted to perform before anyone else reasonably could" [6].

Zewail's work was now focused in two directions: (1) studies of coherence and dynamics of isolated molecules in supersonic beams and (2) development of the optical analogue of NMR spectroscopy. For their "molecular guinea pig" [6] Zewail chose anthracene, $(C_6H_4CH)_2$, a planar molecule consisting of three hexagons fused edge-to-edge, which can vibrate in hundreds of ways and combinations, the frequencies of which were known [79, 80]. After exciting the anthracene molecules into one of those vibrational modes with a laser pulse tuned to that frequency, the researchers counted the picoseconds (10^{-12} s) until the molecule emitted its extra energy by fluorescing. They expected that the fluorescence would decay smoothly as the energy leaked away, which is what occurred—except that several picoseconds later, the fluorescence suddenly reoccurred, spiked, and disappeared again and again for as many as nine times. In Zewail's words,

> Everybody knows we are born, we die, and that's it. But if all of a sudden somebody is coming back from the dead, reincarnated like Shirley MacLaine says, it would be an incredible result. And, of course, some people would be skeptical [6].

Instead of decaying, they observed that the fluorescence was oscillating—what Zewail called "the door-opening observation" [6]. Such oscillations were known in atoms but unexpected in large molecules with a multiplicity of states. According to Zewail,

> Nobody knew it then, but this demonstration of intramolecular coherence was the key to making femtosecond movies. It implied that, under the right conditions, a horde of complex molecules could march in lockstep from a common starting point for a considerable length of time. Thus, a snapshot of any one of those molecules represented them all, and a series of pictures of different molecules taken at different times, when arranged in order, truly was equivalent to a time-lapse movie of a single Joe Average molecule. The inverse-Muybridge problem of synchronizing the gaits of a herd of horses running past a single camera had been solved. So then we said, well, if we can see the vibration, would it be possible to observe the molecule's rotational motion in real time? [6].

In 1986 (John) Spencer Baskin, Peter Felker, and Zewail published the first experimental observations of coherent rotational phenomena in isolated large molecules—using stilbene (diphenylethylene, $C_6H_5CH{=}CHC_6H_5$) [81, 82]. According to Baskin, "With the establishment of rotational coherence on top of vibrational coherence, the creation of a composite molecule was complete" [6], while Zewail recalled, "So it immediately became clear that we had to push the time scale further" [6].

It was fortunate that lasers were also becoming faster. Spectra Physics had recently developed a pulse compressor delivering a 400-femtosecond burst, but because the pulses were becoming so truncated, a dust mote could scatter the beam, and an air current could cause the laser to twinkle. Therefore sliding plastic panels were hung around the optics, and anyone entering Zewail's laboratory, affectionately christened "Femtoland," which was protected from dust by sticky white plastic mats, had to wear blue paper "booties." There are now seven Femtolands (Figure 27).

The Birth of Femtochemistry

Because the lasers had also outpaced the electronics, Zewail, together with graduate student Norbert F. Scherer [83] and postdoctoral fellow Joseph L. Knee [84], developed the pump–probe molecular beam technique—a method that led to the birth of femtochemistry. They used a high-speed camera based on laser technology with light flashes on the order of tens of femtoseconds to observe molecules in the actual course of reactions and take "pictures" of them during the intermediate transition state. The time required for the atoms in a molecule to undergo a single vibration is usually 10 to 100 femtoseconds.

As the Nobel announcement expressed it,

> That chemical reactions should take place on the same scale as when the atoms oscillate in the molecules may be compared to two trapeze artists "reacting" with each other on the time scale as that on which their trapezes swing back and forth. What did the chemists see as the time resolution was successively improved? The first success was the discovery of substances formed along the way from the original one to the final product, substances termed *intermediates*. To begin with these were relatively stable molecules or molecular fragments. Each improvement of the time resolution led to new links in a reaction chain, in the form of increasingly short-lived intermediates, being fitted into the puzzle of understanding how the reaction mechanism worked. The contribution for which Zewail is to receive the Nobel Prize means that we have reached the end of the road: no chemical reactions take place faster than this. With femtosecond spectroscopy we can for the first time observe in "slow motion" what happens as the reaction barrier is crossed and hence also understand the mechanistic background to Arrhenius' formula [63] for temperature dependence and to the formulæ [64] for which van't Hoff was awarded his Nobel Prize [1].

© 2002 Springer-Verlag New York, Inc., S1430-4171(02)02534-6, Published on Web 03/15/2002, 10.1007/s00897020534a, 720100gk.pdf

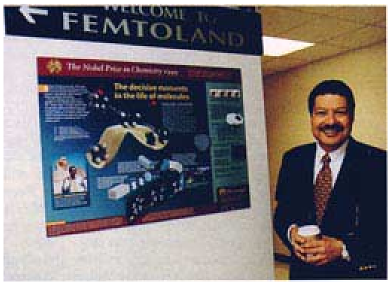

Figure 27. Zewail in a Caltech chemistry building corridor with a Nobel Prize poster and a sign pointing to Femtoland. Reference 20, p 38. (Courtesy, California Institute of Technology.)

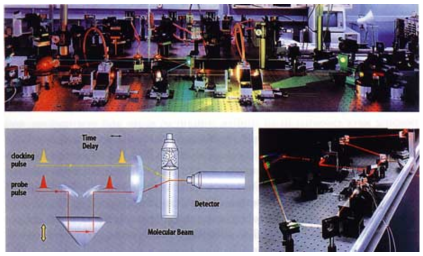

Figure 28. A femtochemistry apparatus typical of early Femtolands. The laser system, the first Colliding Pulse Mode (CPM) oscillator used in Femtoland I (top); the continuum generator (bottom, right); and the experimental layout for clocking (bottom, left). Reference 2, p 117. (Courtesy, the Nobel Foundation.)

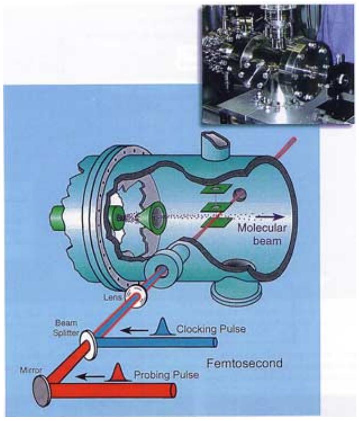

Figure 29. The "World's fastest camera." Molecular-beam apparatus of Femtoland III (top). A beam of molecules is struck by femtosecond pulses of laser light. The pump pulse starts the reaction; the probe pulse "photographs" it (bottom). Reference 2, p 118. (Courtesy, the Nobel Foundation.)

In Zewail's words, "Like the photography used by Muybridge, femtosecond molecular photography also works by breaking up continuous motion into a series of snapshots or frames" [59]. A shutter speed 100 billion times faster than Muybridge's speed is, of course, beyond the reach of any mechanical device so Zewail's "molecular camera" is a combination of ultrafast lasers, a spectroscope, mirrors, prisms, and other optical components. The laser pulse provides the shutter speed for freezing molecular motion with the required spatial resolution, but a well-defined series of measurements, with relative timing accurate to tens of femtoseconds, is needed to record in detail the complete sequence of steps in the process. Also, Muybridge was concerned with only one horse, while millions of molecules, whose motion must be synchronized, are involved in a chemical reaction.

Figure 30. Ahmed H. Zewail with laser apparatus. Reference 20, p 39. (Courtesy, California Institute of Technology.)

All these requirements are satisfied by the pump–probe configuration, which involves two laser pulses (Figures 28–30) [1–3, 6, 60, 62, 85–88]. To make the "molecular movie" the reactants are mixed as molecular beams in a vacuum chamber, and an ultrafast laser is activated and aimed at the target molecules. This first pulse—the pump pulse—strikes a molecule, which absorbs its energy. The reaction is clocked from this instant, which satisfies the requirement of synchronicity and defines the zero of time. If the pulse is tuned to the correct wavelength, corresponding to the energy needed to break the bonds in the molecule, these bonds break, and new species are formed.

Then a weaker pulse—the probe pulse—tuned to the frequency of the bond to be observed is directed through the sample. Its arrival is delayed by a predetermined number of femtoseconds by detouring it through lenses and prisms and making it travel a few microns further than the first pulse, photographing the reaction in progress. According to Zewail,

> The beautiful thing is that the speed of light is so huge—3×10^8 meters per second—that if we move a distance of one micron [10^{-6} m], we can create a delay of 3.3 femtoseconds [6].

In a given experiment the second path was adjusted until both pulses arrived simultaneously at the sample, that is, making the paths exactly equal in length, setting time-zero very accurately, and recording the initial configuration of the molecules. A precision-driven worm gear then eased a mirrored prism slightly further away on the second path. A distance of 30 microns equals about 100 femtoseconds, which was approximately the resolution of the Zewail's group's first experiment, performed in 1985, not yet fast enough to characterize the transition state but fast enough to view the appearance of the product [89].

In this experiment Zewail, Scherer, and Knee, along with former graduate student Duane D. Smith, then a professor at Purdue University, studied the unimolecular decomposition of cyanogen iodide (iodocyanide):

$$\mathrm{ICN} \rightarrow \mathrm{CN} + \mathrm{I}$$

Their first "snapshot" of six frames showed a significant buildup of nascent cyanide radical.

Eventually, the state of the molecular system at any time during the chemical reaction could be identified from the spectrum of light absorbed or emitted by the atoms and molecules struck by the laser beam—a "fingerprint", so to speak—recorded by the spectroscope. The series of changes in spectra from one time to another form a "movie" showing the atoms and molecules in motion. The "fingerprint" and the time elapsing are compared with theoretical simulations based on results of quantum chemical calculations [90] of spectra and energies for the molecules in their various states. Recording the state of molecules at different time intervals allowed Zewail to reconstruct and study the images of simple reactions in real time.

By 1987 the next-generation lasers were able to deliver 50-femtosecond or less pulses, allowing Zewail and graduate student Marcos Dantus and postdoctoral fellow Mark J. Rosker to detect time differences of about one-fifth the pulse width, which made 10-femtosecond resolution a reality [91]. They "photographed" the dissociation reaction at 10-femtosecond intervals, a "shutter speed" fast enough to record about a dozen frames showing the formation of the I···CN transition state, in which the I–CN bond was in the process of breaking little by little. This was the first time that such an event had been "seen" in real time. Using a pump pulse at 306 nm (1 nm = 10^{-9} m) wavelength and a probe pulse at 388.9 nm, they found that the entire reaction required 200 femtoseconds (Figure 31).

"Those were thrilling moments," Zewail said in recalling this crucial experiment. The Caltech faculty recognized the significance of this work. On graduating, Dantus was awarded the Clauser Prize, awarded annually "to the PhD candidate whose research is judged to exhibit the greatest degree of originality as evidenced by its potential for opening up new avenues of human thought and endeavor as well as by the ingenuity with which it has been carried out" [6].

The referee who reviewed the communication for the *Journal of Chemical Physics* (received June 3, 1987; accepted June 15, 1987) was not only prompt but also visionary:

> It has the smell that the authors are onto some very exciting new stuff….This manuscript meets all the requirements for a communication. It may turn out to be a classic. Publish with all dispatch [2].

Zewail's "molecular movies" were immediately recognized not only by the scientific press and science writers, such as Isaac Asimov, Hans Christian von Baeyer, Gary Taubes, and Philip Ball, but by the popular press as well, with significant pieces in newspapers and magazines such as the *New York Times*, *Los Angeles Times, Discover*, etc. and headlines such as "Laser captures 'molecular birth'." *Science* magazine proclaimed,

> By using femtosecond laser pulses chemists can for the first time watch molecules in the act of formation or fragmentation, thus yielding insights into the most crucial component of all chemical reactions, the transition state [85]

and quoted Zewail as saying,

> Observing the instant of a molecule's creation is for a chemist what observing the Big Bang would be for an astronomer [85].

Many monographs and textbooks cited his 1987 discovery and continue to do so. Femtochemistry quickly became a recognized and active area of research, and on March 1–4, 1993 the First International Conference on the field was held in Berlin (Figure 32).

Femtochemical Studies

Through the years Zewail and his students, postdocs, and colleagues have carried out hundreds of pioneering studies of reactions from all branches of chemistry in the field that he almost single-handedly developed [92, 93]. In the words of Professor Bengt Nordén, member of the Royal Swedish Academy of Sciences and of the Nobel Committee for Chemistry,

> Zewail's use of the fast laser technique can be likened to Galilei's use of his telescope, which he directed towards everything that lit up the vault of heaven. Zewail tried his femtosecond laser on literally everything that moved in the world of molecules. He turned his telescope toward the frontiers of science [5].

Here, because of space limitations, we shall mention only those contributions that the Nobel Prize announcement specifically cited [1].

Not every dissociation reaction is as fast as that of ICN. With Rosker and postdoctoral fellow Todd S. Rose, Zewail studied the dissociation of sodium iodide [94],

$$\mathrm{NaI} \rightarrow \mathrm{Na} + \mathrm{I}$$

an experimental system that was a favorite of Linus Pauling's and that Zewail called, "the *Drosophila* of our field" [6]. They used the pump pulse to excite the ion pair Na^+I^- (held together by electrostatic attraction), which has an equilibrium distance of 2.8 Å (1 Ångström unit = 10^{-10} m) between nuclei, to an activated form [NaI]*, which then assumes covalent bonding (Figure 33) [1, 6]. However, its properties change as the molecules vibrate. When the nuclei are at their outer turning points—10 to 15 Å apart—the structure is ionic, whereas at short distances it is covalent, that is, the real potential energy surface (PES) is ionic at short range and covalent at greater distances. At a certain point on the vibration cycle—when the nuclei are 6.9 Å apart, there is a great probability that the molecule will fall back to its ground state or decay into sodium and iodine atoms.

This was Zewail's first case to demonstrate the resonance behavior, in real time, of a bond converting from covalent to ionic along the reaction coordinate. From its results, they found the key parameters of its dynamics such as the time of bond breakage, covalent/ionic coupling magnitude, branching of trajectories, and other significant data. During the 1930s Pauling's description of this bond was static and at equilibrium; at the close of the 1980s Zewail was able to describe its dynamics in real time by preparing structures far from equilibrium [2].

According to Zewail,

> For the first time, we could see a chemical bond transforming in real time from covalent to ionic, covalent, ionic, covalent, ionic, covalent, ionic, covalent, ionic—in this case, by the way, they [the sodium and iodine atoms] were in love for about nine or ten cycles before they divorced each other at the end [6].

The results of the NaI experiments caused a paradigm shift in Zewail's thinking. He then extended his studies to

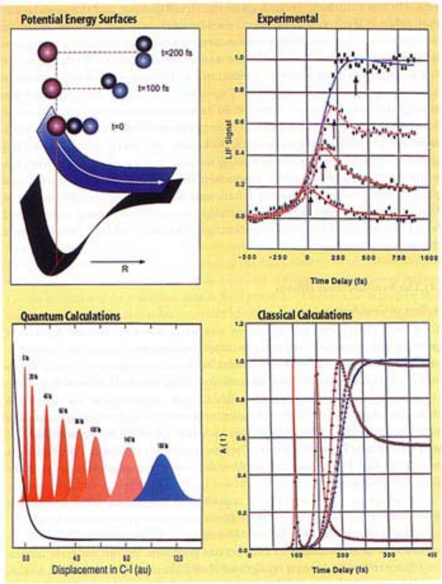

Figure 31. Femtochemistry of the ICN reaction, the first to be studied. The experimental results show the probing of the reaction in the transition-state region (rise and decay) and the final CN fragment (rise and leveling) with precise clocking of the process. The total time is 200 femtoseconds. The I fragment was also detected to elucidate the translational energy change with time. Classical and quantum calculations are shown. Reference 2, p 144. (Courtesy, the Nobel Foundation.)

Figure 32. The First International Conference on Femtochemistry, Berlin, May 1–4, 1993. (Courtesy of Ahmed H. Zewail, biographical collection.)

bimolecular reactions. With Scherer, graduate student Lutfur R. Khundkar, and the late Richard B. Bernstein (1923–1990) of the University of California, Los Angeles, he studied a reaction that occurs in the atmosphere and in combustion:

$$H + CO_2 \rightleftharpoons CO + OH$$

The researchers found that once the hydrogen atom had collided with the oxygen atom of the carbon dioxide molecule, the atoms held together for several picoseconds as they climbed the energy barrier leading to formation of the O–H bond [95]. The O–H bond making and the C–O bond breaking occurred in a nonconcerted manner, and the intermediate HOCO existed for about 1 picosecond (Figure 34). By isolating this transition-state intermediate in real time, they were able to establish the mechanism of the reaction and compare the exact timing to detailed *ab initio* quantum mechanical calculations that theoretical scientists were making from first principles—a rigorous test of the theory [2, 6, 60]. The reaction is the most studied four-atom reaction, both experimentally and theoretically.

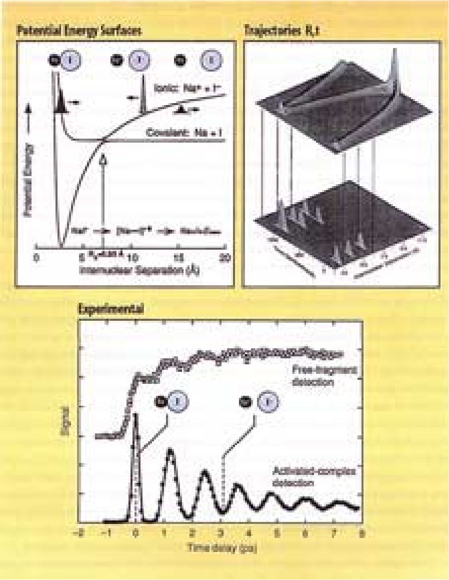

Figure 33. Femtochemistry of the NaI reaction, the paradigm case. The experimental results show the resonance motion between the covalent and ionic structures of the bond as well as the time scales for the reaction and the spreading of the wave packet. Two transients are shown for the activated complexes in transition states and for final fragments. Note the "quantized" behavior of the signal, not simply an exponential rise or decay. The classical motion is simulated as trajectories in space and time (top). Reference 2, p 148. (Courtesy, the Nobel Foundation.)

Khundhar and Zewail [96] used the new technique to answer one of the fundamental questions of chemistry: Why are certain chemical bonds more reactive than others, and if there are two equivalent bonds in one molecule, will they break simultaneously or one at a time? They studied the dissociation of 1,2-tetrafluorodiiodoethane into tetrafluoroethylene (the monomer of teflon, poly(tetrafluoroethylene)) and two iodine atoms by the breaking of two carbon-iodine bonds:

$$F_2IC\text{–}CIF_2 \rightarrow F_2C{=}CF_2 + 2I$$

They found that, although the two C–I bonds are equivalent in the original molecule, they break one at a time rather than simultaneously, with the reaction time of the second carbon-iodine bond breakage being about 17 picoseconds (Figure 35) [2]. The difference in reactivity of the two bonds can be used to control the reaction. Later the structure of the short-lived intermediate radical C_2F_4I was found to be more favorable to the classical radical structure than to the bridged radical structure. They also made *ab initio* calculations to compare theory with their experimental results.

An apparently simple bimolecular reaction studied by Zewail was that between benzene and iodine [1, 97]. When the two molecules approach closely enough, they form a complex. The laser pulse causes an electron to transfer from the benzene molecule to the iodine molecule, which results in the former becoming positively charged and the latter becoming negatively charged. These charges cause the benzene and the nearest iodine atom to attract each other, thus stretching the iodine-iodine bond and causing the other iodine atom to break free (Figure 36). All this occurs within 750 femtoseconds.

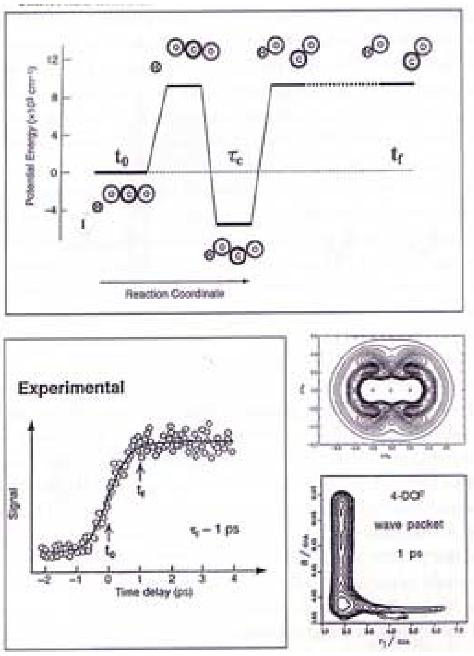

Figure 34. Femtochemistry of the H + CO_2 reaction. The precursor in this molecular beam experiment is HI/CO_2 in a van der Waals complex. The initial experiments utilized picosecond pulses, but later subpicosecond pulses were used. Theoretical *ab initio* calculations of the PES and the dynamics (classical, semiclassical, and quantum wave packet) have all been reported. Reference 2, p 154. (Courtesy, the Nobel Foundation.)

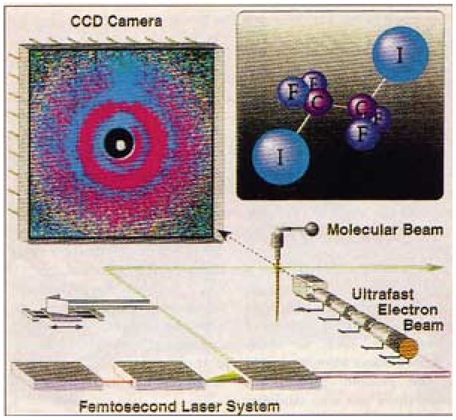

Figure 35. Dissociation of 1,2-tetrafluorodiiodoethane into tetrafluoroethylene and two iodine atoms by the breaking of two carbon–iodine bonds. To detect molecular species by ultrafast diffraction an ultrafast electron pulse strikes a molecular beam to generate a diffraction pattern (top, left). Reference 62, p 162. (Courtesy, California Institute of Technology.)

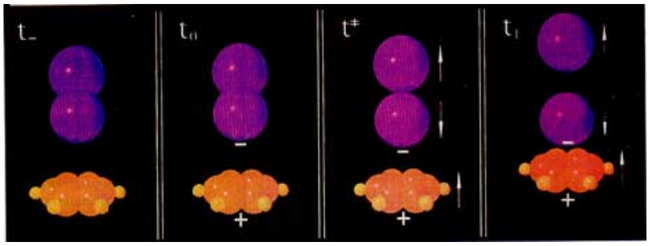

Figure 36. The biomolecular reaction between benzene and iodine. After receiving an electron from benzene (orange) an iodine molecule (purple) undergoes cleavage in 750 femtoseconds. Reference 62, p 157. (Courtesy, California Institute of Technology.)

$$C_6H_6 + I_2 \rightarrow C_6H_6^{+}I_2^{-} \rightarrow C_6H_6.I + I$$

Zewail also found that this is not the only way that iodine atoms can be formed. In some cases the electron falls back onto the benzene molecule. However, by this time the bond between the two atoms breaks, and they fly apart.

Zewail also extended his technique to complex organic reactions and answered questions that chemists have asked for more than a half-century such as: What are the elementary steps and the overall mechanism? What is the nature of the transition state region? How do multiple bonds form and break, concertedly (simultaneously) or nonconcertedly (sequentially)? What is the time scale for the dynamics of different bonds: weak bonds, such as the hydrogen bond, and strong bonds, such as covalent, ionic, or metallic bonds? [60].

A prototypical case investigated by Zewail was the ring opening of cyclobutane to yield ethylene or its reverse—the addition reaction of two ethylene molecules to yield cyclobutane [1, 60]:

$$(CH_2)_4 \rightleftharpoons 2[H_2C{=}CH_2]$$

The reaction may proceed via the concerted (synchronous) approach of two ethylene molecules and formation of one transition state with a simple activation barrier, or it may proceed via a two-stage mechanism in which first one bond breaks, forming tetramethylene as a reactive diradical intermediate consisting of a chain of four singly bonded carbon atoms and two free electrons (Figure 37). After crossing another activation barrier, the tetramethylene is converted into the final product. By femtosecond spectroscopy Zewail found that the intermediate was formed with a lifetime of 700 femtoseconds, many times greater than the vibrational period, indicating the nonconcerted nature of the mechanism and the existence of a quasi-bound species between reactants and products [98].

Another reaction that Zewail and his co-workers studied by femtosecond spectroscopy was the photoisomerization of stilbene (diphenylethylene) (Figure 38) [99]. Ordinarily, because double bonds are rigid and do not spin freely, the two benzene rings should be locked into either the *cis* or *trans* position in the two corresponding isomers. However, Bañaras and Zewail found that during the light-induced conversion the two benzene rings turn synchronously in relation to each other and the entire process is complete in about 300 femtoseconds [6, 99].

Applications

Zewail and others have devised numerous practical applications of femtochemistry, giving rise to femtobiology, femtophysics, and other femtosciences (Figures 39 and 40). For example, at the University of California, Berkeley Richard A. Mathies (b. 1946) and Charles V. Shank (b. 1943), working on biochemical molecules with a double-bonded structure, showed that retinal, the color substance in rhodopsin, a light-sensitive pigment in the rods of the eye, undergoes a reaction similar to the isomerization of stilbene, discussed in the previous paragraph [1, 6]. The primary photochemical step by which the eye perceives light consists of a *cis-trans* isomerization about the double bond in retinal. Using femtosecond spectroscopy, the Berkeley researchers found that

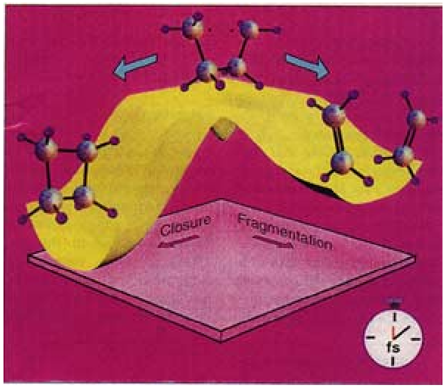

Figure 37. The ring-opening of cyclobutane to yield ethylene or its reverse. When two ethylene molecules (right) combine to form a ring of cyclobutane (left), they pass through a highly unstable transition state (center), from which the reaction may proceed either forward or backward. Reference 62, p 160. (Courtesy, California Institute of Technology.)

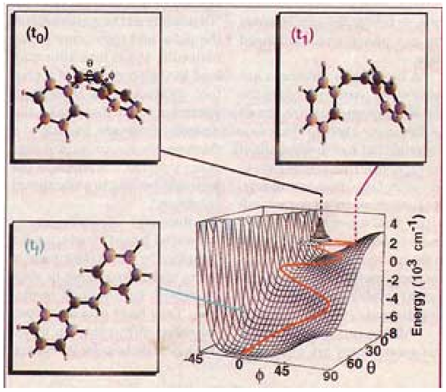

Figure 38. Femtochemistry of the photoisomerization of *cis*-stilbene to *trans*-stilbene. When a femtosecond laser pulse strikes *cis*-stilbene, the central double bond is weakened, permitting rotation of the benzene rings through 90° in ca. 300 femtoseconds. Reference 62, p 161. (Courtesy, California Institute of Technology.)

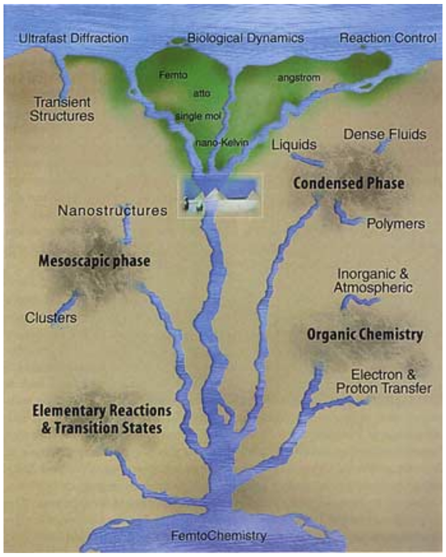

Figure 39. Branches of femtochemistry from the early days of studying elementary reactions and transition states ("southern" part) to current activities ("northern" part). The flow has produced the different branches studied at Caltech. Reference 2, p 162. (Courtesy, California Institute of Technology.)

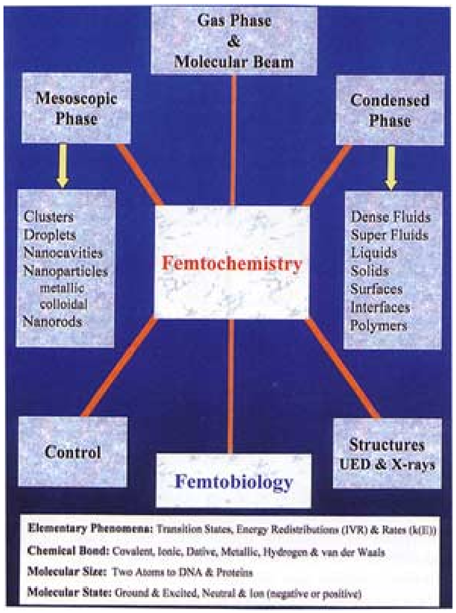

Figure 40. Femtochemistry and the scope of its applications. Reference 2, p 120. (Courtesy, California Institute of Technology.)

this process, which is the first step in transforming a photon of light into a nerve impulse, occurs in 200 femtoseconds with 70 percent efficiency, and a certain amount of vibration remains in the reaction product (Figure 41). The reaction's speed and high efficiency suggest that the incoming light is not first redistributed throughout the molecule but is localized directly to the double bond, thus explaining the eye's good night vision. This localization is a theme that related to Zewail's early studies of coherence, identical in concept to his previously mentioned work on sodium iodide [94]. Another biologically important reaction, for which femtochemistry has explained efficient energy conversion, is photosynthesis, the process by which chlorophyll molecules absorb energy from sunlight. Zewail exclaimed,

> How wonderful that we can now study the structure and dynamics of the chemical bond from simple table salt all the way to complex proteins [62].

Femtosecond investigations following Zewail's work are now being carried out all over the world, using not only molecular beams but also processes on surfaces. These studies permitted an understanding and improvement of catalysts, an understanding of the mechanisms of dissolving substances and of their reactions in solution, and development of new polymeric materials for use in electronics [1].

Knowledge of chemical reaction mechanisms can also be used to control these reactions. A given reaction is frequently accompanied by undesirable, competing reactions that lead to a mixture of products, thus requiring separation of undesirable by-products. If the reaction can be controlled by initiating reactivity in selected bonds, such separations and purifications could be rendered unnecessary. As early as 1980 Zewail anticipated this possibility in an article on laser-selective chemistry [100]. In his words,

> The control of chemical reactions through the initiation of reactivity of selected bonds would [reduce waste and unintended products]. It is indeed exciting to reach the stage of this new thinking about manipulating matter [62].

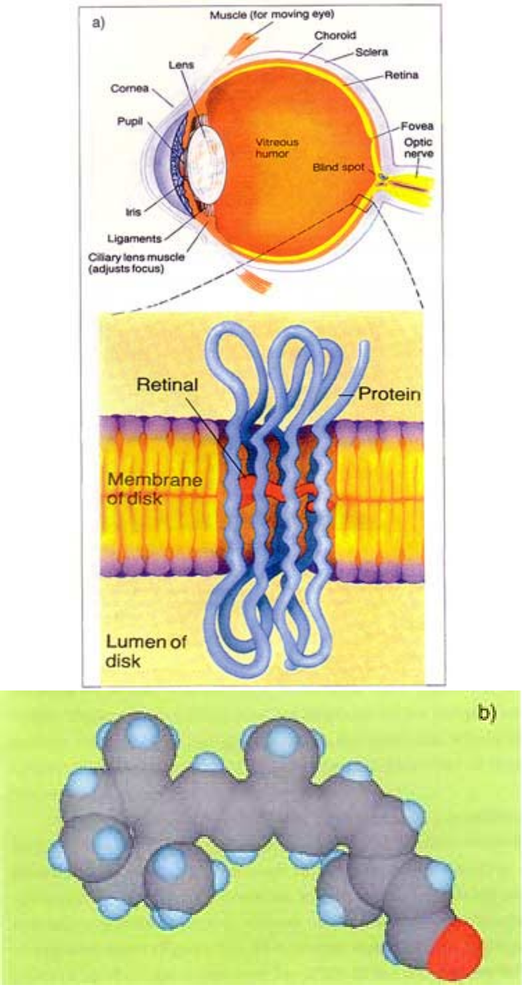

Figure 41. (a) The first step in vision, which is the result of the conversion of light energy to an electrochemical impulse transmitted, through neurons, to the brain. Rhodopsin, one of the initial receptors, is a pigment in the rods of the retina. It consists of retinal, an organic molecule, in association with a protein, opsin. (b) The isomerization of the retinal backbone makes it more linear and gives opsin the signal to undergo a sequence of dark (thermal) reactions involved in triggering neural excitation. Reference 60, p 69. (Courtesy, California Institute of Technology.)

Zewail has asked,

> Can we actually take a direct structural image of a molecule as it undergoes these transitions, using femtosecond electron diffraction? Once we break a bond here or a bond there, how does the architecture of this molecule change with time? This is a dream that I have shared with some members of my group since 1991, and it has become a major effort lately [6].

In the 1990s Zewail and his co-workers showed for the first time that they could actually see the chemical structure of the entire molecule in a simple model system on a picosecond time scale. They used a technique called ultrafast electron diffraction, which yields the three-dimensional location of all the atoms in the molecule, regardless of its size [101], in Zewail's words, "just like a chest X-ray" [6]. In discussing this new technique, he stated,

> When we look at a molecule's diffraction pattern we can "see" the structure. Our ultimate goal is to see how the atoms move as they perform a biological function. You can imagine watching a protein, for example, moving around as it catalyzes a reaction, or as it recognizes and binds to an antibody. With diffraction you see the entire ensemble at once, in real time. You can see why I'm so excited [6].

He also said,

> Once we understand how molecules are formed, we can manipulate them. If you can manipulate molecules, you can manipulate genes and matter, you can synthesize new material—the implications are just unbelievable [43].

The Future of Femtochemistry

Since femtosecond resolution now provides the limit for time resolution for phenomena involving nuclear motion, in the future attosecond (10^{-18} s, from the Danish-Norwegian *atten*, "eighteen") resolution [102] may allow direct observation of the motion of electrons, a prediction that Zewail made in a review in 1991 [103]. Recently, Austrian physicists at the Technische Universität Wien (Vienna University of Technology) Photonics Institute irradiated neon with bursts of red light lasting only 7 femtoseconds, which stripped electrons from the gas atoms and resulted in harmonic pulses of extreme ultraviolet and X-ray light with much higher frequencies than that of the red light [104]. After filtering the harmonic light so as to allow only select attosecond bursts of X-rays to pass, they trained the red light and X-rays onto a krypton target and were able to monitor the dynamics of photoelectrons emitted by the krypton with attosecond resolution. In Zewail's words [105], "These are the kind of exciting developments that take us into new territory."

For example, in coming decades the arrangements of the electrons in benzene might be observed in real time [60]. According to Zewail [6, 106],

> It seems that on the femtosecond to attosecond time scale we are reaching the "inverse" of the big bang time (Figure 42), with the human heartbeat "enjoying" the geometric average of the two limits—perhaps we are approaching a universal limit! The language of molecular dynamics is even similar to that of cosmos dynamics. Cosmologists are speaking of energy landscapes and transition states for the big bang and universe inflation!

In another recent breakthrough Zewail and his co-workers used the new ultrafast electron diffraction technique to probe the evolving structure of an excited molecule as it decays and in so doing discovered a hitherto unknown structural intermediate [107]. They showed that a pyridine molecule, when excited into a special state, unexpectedly sheds its excess energy by opening its ring [108]. Zewail stated, "None of us anticipated opening of the ring" [107]. Although ordinary electron diffraction gives distances between nuclei and thus reveals the structure of a compound, Zewail's method repeatedly takes "snapshots" of a reacting system every fraction of a picosecond. In his words, "It's so clean and neat—usually experiments don't cooperate like this" [107]. According to A. Welford Castleman, Jr. [107],

> The ability to directly observe the breakage of bonds and the formation of new ones opens up a new approach to the study of wide classes of chemical and photochemical processes.

Zewail's group intends to investigate many more reactions and is constructing another generation of ultrafast electron diffraction instruments to perform experiments in the

© 2002 Springer-Verlag New York, Inc., S1430-4171(02)02534-6, Published on Web 03/15/2002, 10.1007/s00897020534a, 720100gk.pdf

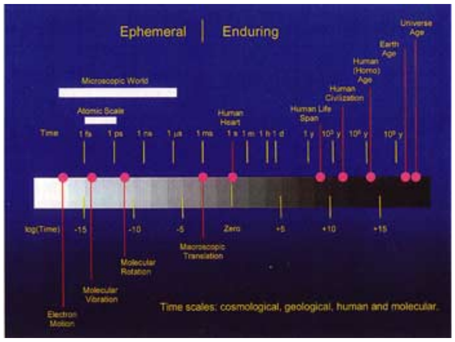

Figure 42. The time scales of cosmological, geological, human, and molecular events, which span more than 30 orders of magnitude, from the big bang to the femto age. Reference 2, p 189. (Courtesy, the Nobel Foundation.)

condensed phase and on biological systems. He exclaims, "This is going to keep us excited for many years to come" [107].

Major advances in biology and medicine might include the study and control of enzymatic reactions and the catalytic nature of the transition state. Also, the recording of a large biological structure changing with time and with atomic resolution may become possible and prove useful in problems involving protein folding and molecular recognition. Among medical applications pulsed and time-resolved transillumination imaging techniques have already been used for applications in tomography. Time-resolved imaging of cancer tumors, currently with picosecond resolution, and femtosecond two-photon microscopy are now common [60].

In the words of the Nobel Prize announcement,

> Femtochemistry has fundamentally changed our view of chemical reactions. From a phenomenon described in relatively vague metaphors such as "activation" and "transition state," we can now see the movements of individual atoms as we imagine them. They are no longer invisible. Here lies the reason why the femtochemistry research initiated by this year's Nobel Laureate has led to explosive development. With the world's fastest camera available, only the imagination sets bounds for new problems to tackle [1].

Epilogue

Despite his celebrity and the demands on his time that are an invariable concomitant of the receipt of a Nobel Prize, Zewail is determined that the prize will not interfere with his work:

> I'm still young, and there are plenty of things I want to do with my group. We are hoping to be able to study molecular transformations of complex systems, particularly DNA and proteins [10].

Zewail's Nobel lecture masterly surveys the field of femtochemistry, which he almost single-handedly created, "from a personal perspective, encompassing [his group's] research at Caltech and focusing on the evolution of techniques, concepts, and new discoveries" [3]. He concluded it with his views of the nature of science and discovery, using quotations involving the two nations and cultures to which he belongs. First, Egypt:

> What is clear to me is that my group and I have enjoyed the odyssey of discovery, seeing what was not previously possible, acquiring new knowledge and developing new concepts. Perhaps the best words to describe this feeling are those of the English archæologist, Howard Carter, on November 25th 1922 when he got his first glimpse of the priceless contents of Tutankhamen's Tomb—*At first, I could see nothing,…then shapes gradually began to emerge*….Lord Carnarvon, who financed the excavation of this discovery, asked, when looking with Carter, *What do you see?* Carter replied, *"Beautiful Things, Beautiful Things."* This is the thrill of discovery, too. It seeks to unveil the hidden simplicity and beauty of Nature's truth [2].

Second, the United States:

> The future of femtoscience will surely witness many imaginative and unpredictable contributions. I hope that I will be able to enjoy the future as much as I have the past. Benjamin Franklin once wrote: *"The progress of human knowledge will be rapid and discoveries made of which we at present have no conception. I begin to be almost sorry I was born so soon since I cannot have the happiness of knowing what will be known in years hence"* [2, 3].

Acknowledgments. We are indebted to University Photographer Randy Vaughn-Dotta of the California State University, Fresno Academic Innovation Center for his excellent photographic work; Reference Librarians Diane Majors and Thomas Zimoski of the CSUF Henry Miller Madden Library and Fresno County Library, respectively, for locating source material; Kristina Fallenius of Nobelstiftelsen (the Nobel Foundation) for copies of the 1999 Nobel Prize in Chemistry lecture, biographical sketch, and presentation speech; and Research Corporation of Tucson, Arizona for financial support.

References and Notes

1. The Nobel Prize in Chemistry 1999. http://www.nobel.se/announcement-99/chemistry99.html (accessed Jan 2002).
2. Zewail, A. H. Femtochemistry: Atomic Scale Dynamics of the Chemical Bond using Ultrafast Lasers, Nobel Lecture, Dec.10, 1999, and Biographical Sketch. In *Les Prix Nobel 1999;* The Nobel Foundation: Stockholm, 2000.
3. Zewail, A. H. Femtochemistry: Atomic-Scale Dynamics of the Chemical Bond, adapted from his Nobel Lecture. *J. Phys. Chem. A* **2000,** *104* (24), 5610–5694; http://pubs.acs.org/CHECKCCIP-961478933/isubscribe/journals/jpcafh/jtext.cgi?jpcafh/1 (accessed Jan 2002, requires subscription).
4. Penn Chemistry Alum Wins Nobel Prize. *The Penn Alchemist* **2000,** *23* (Spring), 4–5.
5. Nordén, B. The Nobel Prize in Chemistry: The Work of Professor Ahmed H. Zewail, presentation speech. In *Nobel Priset: The Nobel Prize, Translation of the Speeches at the 1999 Prize Award Ceremony;* The Nobel Foundation: Stockholm, 1999, pp 17–22.
6. Smith, D. L. Coherent Thinking. Engineering & Science (California Institute of Technology) **1999,** 62 (4), 7–17.
7. Bradley, D. Singling out Nobel Molecules. *The Alchemist*: News, October 22, 1999; http://chemweb.com/alchem/1999/news/nw_991012_zewail.html (accessed Jan 2002, requires ChemWeb login).
8. Bradley, D. Molecular Strobe Lighting Wins Nobel Prize. *The Alchemist*: Catalyst, October 22, 1999; http://chemweb.com/alchem/1999/catalyst/ct_991015_nobel.html (requires ChemWeb login).
9. Dagani, R. Zewail: Glimpses of the Ultrafast. *Chem. Eng. News* **1999,** *77* (42), 12–13.
10. Collier, D. Transition State Study Earns Nobel Award. *Chem. & Ind.* **1999**, *21* (Nov 1), 828.

© 2002 Springer-Verlag New York, Inc., S1430-4171(02)02534-6, Published on Web 03/15/2002, 10.1007/s00897020534a, 720100gk.pdf

11. Chemistry: Egyptian Snaps Up Nobel Prize. *Chem. & Ind.* **1999**, *20* (Oct 18), 779.
12. Alumni Profiles: Class of '74: Nobelist Found a Way to Peer into the World of Molecules. *The Pennsylvania Gazette* **2000** (Jan/Feb), 60–61.
13. Brubacher, L. J. 1999 Nobel Prizes. *CHEM 13 NEWS* **1999**, *279* (Nov), 12.
14. Verrengia, J. B. Egyptian-American Awarded Nobel Prize. *The Fresno Bee*, October 13, 1999, p A6.
15. Gwynne, P. Chemistry with a Light Touch. *Chemistry (American Chemical Society)* **1999** (Fall), 8–10.
16. Nobel Award Winners Think Small. *The Ottawa Citizen*, October 13, 1999, p A9.
17. Isa, M. Dutch Physicists, Egyptian Chemist Win Nobel Prizes. *The Toronto Star*, Edition 1, News, October 13, 1999.
18. Weiss, K. R. Caltech's Nobel Tradition Continues; Chemistry: Ahmed Zewail Becomes the University's 28th Prize-Winner, Earning the Honor for His Work with High-Speed Lasers. *Los Angeles Times*, October 13, 1999, Metro, Part B, p 1.
19. Fordahl, M. Caltech Professor Wins Nobel Prize in Chemistry. *The Association Press State & Local Wire*, October 13, 1999, State and Regional.
20. Rawls, R. L. Ahmed Zewail's Dynamic Chemistry. *Chem. Eng. News* **2000**, *78* (21), 35–39.
21. Peterson, I. Chemistry Nobel Spotlights Fast Reactions. *Science News* **1999**, *156* (Oct 16), 247.
22. Bhaskaran, H. Up Front: Femtosecond Scientist Gets Real-Time Wakeup Call from Stockholm. *Caltech News* **1999,** *33* (3), 2–11.
23. Stevenson, R. The Ultimate Slo-Mo Reply: Studies of Reaction Dynamics Have Reached the Pinnacle in Terms of Time Resolution, Thanks to the Work of This Year's Nobel Prizewinner in Chemistry. *Chem. Br.* **1999,** *35* (11), 24–25.
24. Bradley, D. Flash of Inspiration Wins Nobel Prize for Chemistry. *Educ. Chem.* **2000,** *37* (1), 8.
25. The Nobel Prizes for 1999: Chemistry: The Femtosecond Camera Shutter. *Scientific American* **2000***, 282* (1), 15.
26. Service, R. F. Nobel Prizes: Colleagues Say "Amen" to This Year's Choices: Chemistry: A Winning Dance. *Science* **1999**, *286* (Oct 22), 667, 669.
27. Chemistry in the News: 1999 Nobel Prize in Chemistry. *J. Chem. Educ.* **2000**, *77* (1), 14–15.
28. Reese, K. M. Newscripts: Nobels' value to rise. *Chem. Eng. News* **2000,** *78* (5), 56.
29. Kauffman, G. B.; Kauffman, L. M. George Andrew Olah: An Interview with the 1994 Nobel Chemistry Laureate. *Chem. Intelligencer* **1995,** *1* (2), 6–13; George Olah: Nobel Superchemist. *Today's Chemist at Work* **1995,** *4* (8), 53–54, 72; The Master of Hydrocarbons. *The World & I* **1995,** *10* (9), 168–175.
30. Van Houten, J. C. Review of the One Hundred Year History of Nobel Prizes in Chemical Dynamics. 221st National Meeting, American Chemical Society, San Diego, CA, April 1–5, 2001, CHED 120; Chemical Dynamics at the Turn of the New Century: Nobel Laureates Look Back and Ahead. *J. Chem. Educ.* **2001,** *78,* 860.
31. Biographical Sketch: Ahmed H. Zewail. http://www.its.caltech.edu/~femto/zewail.html (accessed Jan 2002).
32. *Who's Who in America,* 54th (Millenium) ed.; Marquis Who's Who: New Providence, NJ, 2000; Vol. 2, p 5450.
33. *American Men & Women of Science,* 19th ed.; R. R. Bowker: New Providence, NJ, 1995–96; Vol. 7, p 1064.
34. Partington, J. R. *A Short History of Chemistry*; 3rd ed.; Harper & Brothers: New York, 1960; pp 19–20. Contrary to a prevalent misconception, the term "chemistry" never had the meaning of a "black art" as applied to magic. Rather it probably meant "the Egyptian art."
35. Issa, R. M.; El-Ezaby, M. S.; Zewail, A. H. Spectrophotometric Studies of Some Dihydroxyanthraquinones in Aqueous Solutions. *Z. Phys. Chem.* **1970,** *B 244,* 155; El-Ezaby, M. S.; Salem, T. M.; Zewail, A. H.; Issa, R. M. Spectral Studies of Some Hydroxy Derivatives of Anthraquinones. *J. Chem. Soc.* **1970,** *B 7,* 1293; Issa, R. M.; Zewail, A. H. Spectrophotometric Studies on Purpurine and Quinalizarin in Aqueous Solutions. *Egypt. J. Chem.* **1971,** *14,* 461; Issa, R. M.; Ahmed, Y. Z.; Zewail, A. H. Infrared Spectrophotometric Study of Some Hydroxyanthraquinones and Their Sodium Salts. *Egypt. J. Chem.* **1972**, *15*, 1.
36. Coontz, Jr., R. J. Horsefeathers: Scientific prefixes borrow a page from the Marx brothers. *The Sciences* **1994,** *34* (Nov/Dec), 12.
37. Hochstrasser, R. M.; Wessel, J. E.; Zewail, A. H. Zeeman Effect Studies of the Triplet States of Benzene on the Singlet $n\pi^*$ State of S-Triazine. *J. Chem. Phys.* **1971,** *55,* 3596–3597.
38. Hochstrasser, R. M.; Zewail, A. H. Optical Spectroscopic Determination of the Zero-Field Splitting in Vibronic Levels of the Triplet State of Nitrite. *J. Chem. Phys.* **1971,** *54,* 2979–2981; Hochstrasser, R. M.; Wessel, J. E.; Whiteman, J. D.; Zewail, A. H. Characterization of Triplet States of Axially Symmetric Benzenes Using the Zeeman Effect. *Chem. Phys. Lett.* **1971,** *10,* 452–454.
39. Nishimura, A. M.; Zewail, A. H.; Harris, C. B. Zero Field Optically Detected Magnetic Resonance of Multiple Localized States in 1,4-Dibromonaphthalene Crystals. *J. Chem. Phys.* **1975,** *63,* 1919–1923.
40. Zewail, A. H.; Harris, C. B. Coherence in Electronically Excited Dimers. I. The Observation of Coherent Dimers and Its Relationship to Coherent Excitons. *Chem. Phys. Lett.* **1974,** *28,* 8–14; Zewail, A. H.; Harris, C. B. Coherence in Electronically Excited Dimers. II. Theory and Its Relationship to Exciton Dynamics. *Phys. Rev.* **1975,** *B 11,* 935–951; Zewail, A. H.; Harris, C. B. Coherence in Electronically Excited Dimers. III. The Observation of Coherence in Dimers Using Optically Detected Electron Spin Resonance in Zero Field and Its Relationship to Coherence in One-Dimensional Excitons. *Phys. Rev.* **1975,** *B 11,* 952–963.
41. Zewail, A. H. Triplet Exciton Band Structure of Crystalline Phenazine. *Chem. Phys. Lett.* **1974,** *29,* 630–632; Zewail, A. H. Coherence in the Excited States of Multidimensional Systems: Dimer and Exciton Dynamics in Crystalline Phenazine. *Chem. Phys. Lett.* **1975,** *33,* 46–52.
42. Lewellyn, M. T.; Zewail, A. H.; Harris, C. B. Energy Transfer in One-Dimensional Molecular Crystals: Direct and Indirect Energy Exchange in the Non-Boltzmann Regime. *J. Chem. Phys.* **1975,** *63,* 3687–3693; Shelby, R. M.; Zewail, A. H.; Harris, C. B. Coherent Energy Migration in Solids: Determination of the Average Coherence Length in One-Dimensional Systems Using Tunable Dye Lasers. *Chem. Phys. Lett.* **1976,** *64,* 3192–3203.
43. Barber, M. Getting One Award after Another; Egypt-Born Scientist Hits Fast Track in U.S. *Los Angeles Times*, July 22, 1989, Part 1, p 29, col. 1.
44. Mekay, E. Survey—Egypt: Tide of Emigrants Is Turning Back: The Return of the Youth. *Financial Times (London),* May 10, 2000, p 17.
45. Frank, L. A Biotech Gambit in the Desert. *Science* **2001,** *292,* 1478.
46. Zewail, A. H., Ed. *Advances in Laser Spectroscopy,* Vol. 1; SPIE Publishing Co.: Bellingham, WA, 1977.
47. Zewail, A. H., Ed. *Advances in Laser Chemistry,* Vol. 3; Springer Series in Chemical Physics; Springer-Verlag: New York, 1978.
48. Zewail, A. H., Ed. *Photochemistry and Photobiology, Proceedings of an International Conference,* Vols. I and II; Harwood Academic Publishers: New York; London; Chur, Switzerland, 1983.
49. Harris, C. B.; Zewail, A. H.; Ippen, E. P.; Mourou, G. A., Eds. *Ultrafast Phenomena VII: Proceedings of the 7th International Conference, Monterey, CA, May 14-17, 1990;* Springer Series in Chemical Physics 53; Springer-Verlag: Berlin, New York, 1990.
50. Zewail, A. H., Ed. *The Chemical Bond: Structure and Dynamics;* Academic Press: Boston, MA, 1992.
51. Martin, J.-L.; Zewail, A. H.; Migus, A.; Mourou, G. A., Eds. *Ultrafast Phenomena VIII: Proceedings of the 8th International*

Conference, Antibes Juan-les-Pins, France, June 8-12, 1992; Springer Series in Chemical Physics 55; Springer-Verlag: Berlin, New York, 1994.

52. Barbara, P. F.; Zewail, A. H.; Knox, W.; Mourou, G. A., Eds. *Ultrafast Phenomena IX: Proceedings of the 9th International Conference, Dana Point, CA, May 2–6, 1994*; Springer Series in Chemical Physics 60; Springer-Verlag: Berlin, New York, 1994.
53. Zewail, A. H. *Femtochemistry—Ultrafast Dynamics of the Chemical Bond;* World Scientific Publishing Co.: Singapore; River Edge, NJ, 1994; 2 Vols.
54. Seife, C. Science and Religion Advance Together at Pontifical Academy. *Science* **2001,** *291,* 1472–1474.
55. Zewail, A. H.; Batchelder, J. S. Solar Energy Concentrator Devices; U.S. Patent 4,227,939; October 14, 1980.
56. *American Chemical Society Awards, 2000 Edition*; American Chemical Society: Washington, DC, 2000; pp 37, 48, 54.
57. People in the News. *Los Angeles Times*, June 15, 1989; San Gabriel Valley, Part 9, p 9, col. 5.
58. People in the News. *Los Angeles Times*, June 27, 1993; San Gabriel Valley, Part J, p 3, col. 1.
59. Dantus, M. New Voices in Chemistry: Laser Control of Chemical Reactions. *Chem. Eng. News* **2001,** *79* (13), 191.
60. Baskin, J. S.; Zewail, A. H. Freezing Time—in a Femtosecond: In Femtoscience Microscopic Motion Is Filmed in a Millionth of a Billionth of a Second. *Science Spectra* **1998,** *14*, 62–71.
61. Laidler, K. J. *To Light Such a Candle: Chapters in the History of Science and Technology;* Oxford University Press: Oxford, England, New York, 1998; pp 101–106.
62. Jain, V. K. The World's Fastest Camera. *The World & I* **1995**, *10* (10), 156–163.
63. Arrhenius, S. Chemische Reaktionsgeschwindigkeiten. *Z. physik. Chem.* **1899,** *28,* 317–335.
64. van't Hoff, J. H. In *Etudes de Dynamiques Chimiques;* F. Muller: Amsterdam, 1884; p 114.
65. Levine, R. D.; Bernstein, R. B. *Molecular Reaction Dynamics and Chemical Reactivity;* Oxford University Press: Oxford, 1987.
66. Kauffman, G. B. Tío Enrique, el pequeño Mexicano: Henry Eyring (1901–1981). *Anuario Latinoamericano de Educación Química (San Luis, Argentina)* **1998–1999**, *11* (11), 15–19; Henry Eyring (1901–1981). In *American National Biography;* Garraty, J. A.; Carnes, M. C., Eds.; Oxford University Press: Oxford, England, New York, 1999; Vol. 7, pp 654-656.
67. Eyring, H.; Polanyi, M. Einfache Gasreaktionen. *Z. physik. Chem. B* **1931,** *12,* 279–311; Polanyi, M. *Atomic Reactions;* Williams and Norgate: London, 1932.
68. Zewail, A. H.; Bernstein, R. B. Real-Time Laser Femtochemistry. Viewing the Transition from Reagents to Products. *Chem. Eng. News* **1988,** *66* (45), 24–43; Zewail, A. H., Ed. *The Chemical Bond: Structure and Dynamics;* Academic Press: Boston, MA, 1992; p 223 *et seq.*
69. Norrish, R. G. W.; Porter, G. Letters to the Editors: Chemical Reactions Produced by Very High Light Intensities. *Nature* **1949,** *164,* 658; Norrish, R. G. W. Some Fast Reactions in Gases Studied by Flash Photolysis and Kinetic Spectroscopy. In *Nobel Lectures Including Presentation Speeches and Laureates' Biographies. Chemistry 1963–1970;* Elsevier Publishing Co.: Amsterdam-London-New York, 1972; pp 206–238.
70. Porter, G. Flash Photolysis and Some of Its Applications. In *Nobel Lectures Including Presentation Speeches and Laureates' Biographies. Chemistry 1963–1970;* Elsevier Publishing Co.: Amsterdam-London-New York, 1972; pp 241–263.
71. Eigen, M. Ionic Reactions in Aqueous Solutions with Half-times as Short as 10^{-9} Second. Applications to Neutralization and Hydrolysis Reactions. *Discuss. Faraday Soc.* **1954,** *17,* 194–205; Immeasurably Fast Reactions. In *Nobel Lectures Including Presentation Speeches and Laureates' Biographies. Chemistry 1963–1970;* Elsevier Publishing Co.: Amsterdam-London-New York, 1972; p 170–203.
72. Herschbach, D. R. Molecular Dynamics of Elementary Chemical Reactions. *Angew. Chem. Int. Ed. Engl.* **1987,** *26,* 1221–1243; In *Nobel Lectures Including Presentation Speeches and Laureates' Biographies. Chemistry 1981–1990;* Malmström, B. G., Ed.; World Scientific Publishing Co.: Singapore-River Edge, NJ-London-Hong Kong, 1992; pp 265–314.
73. Lee, Y. T. Molecular Beam Studies of Elementary Chemical Processes. *Science* **1987,** *236,* 793–798; In *Nobel Lectures Including Presentation Speeches and Laureates' Biographies. Chemistry 1981–1990;* Malmström, B. G., Ed.; World Scientific Publishing Co.: Singapore-River Edge, NJ-London-Hong Kong, 1992; pp 320–354.
74. Polanyi, J. C. Some Concepts in Reaction Dynamics. In *Nobel Lectures Including Presentation Speeches and Laureates' Biographies. Chemistry 1981–1990;* Malmström, B. G., Ed.; World Scientific Publishing Co.: Singapore-River Edge, NJ-London-Hong Kong, 1992; pp 359–407.
75. Zare, R. N.; Bernstein, R. B. State-to-state Reaction Dynamics. *Phys. Today* **1980,** *33* (11), 43–50; Alexander, A. J.; Zare, R. N. Anatomy of Elementary Chemical Reactions. *J. Chem. Educ.* **1998,** *75,* 1105–1118.
76. Zewail, A. H.; Orlowski, T. E.; Dawson, D. R. Incoherent Resonance Decay and Coherent Optical Ringing from Coherently Prepared Electronic States: A New Technique for Probing Phase Memory and Radiationless Relaxation in Gases and Solids. *Chem. Phys. Lett.* **1976,** *44,* 379–384.
77. Zewail; A. H.; Orlowski, T. E. Optical Ringing in Solids: The Observation of Optical Coherence and Resonance Decay from Selectively Prepared Molecular Packets in Molecular Crystals. *Chem. Phys. Lett.* **1977,** *45,* 399–403.
78. Zewail, A. H.; Orlowski, T. E.; Jones, K. E. Radiationless Relaxation in "Large" Molecules: Experimental Evidence for the Preparation of True Molecular Eigenstates and Born-Oppenheimer States by a Coherent Light Source. *Proc. Nat. Acad. Sci.* **1977,** *74,* 1310–1314.
79. Lambert, W. R.; Felker, P. M.; Zewail, A. H. Quantum Beats and Dephasing in Isolated Large Molecules Cooled by Supersonic Jet Expansion and Excited by Picosecond Pulses: Anthracene. *J. Chem. Phys.* **1981,** *75,* 5958–5960; Picosecond Excitation and Selective Intramolecular Rates in Supersonic Molecular Beams. I. SVL Fluorescence Spectra and Lifetimes of Anthracene and Deuterated Anthracenes. *J. Chem. Phys.* **1984,** *81,* 2209–2216.
80. Lambert, W. R.; Felker, P. M.; Syage, J. A.; Zewail, A. H. Jet Spectroscopy of Anthracene and Deuterated Anthracenes. *J. Chem. Phys.* **1984,** *81,* 2195–2208.
81. Baskin, J. S.; Felker, P. M.; Zewail, A. H. Doppler–Free Time-Resolved Polarization Spectroscopy of Large Molecules: Measurement of Excited State Rotational Constants. *J. Chem. Phys.* **1986,** *84,* 4708–4710.
82. Felker, P. M.; Baskin, J. S.; Zewail, A. H. Rephasing of Collisionless Molecular Rotational Coherence in Large Molecules. *J. Phys. Chem.* **1986,** *90,* 724–728.
83. Perry, J. W.; Scherer, N. F.; Zewail, A. H. Picosecond Pump–Probe Multiphoton Ionization of Isolated Molecules: IVR and Coherence. *Chem. Phys. Lett.* **1983,** *103,* 1–8; Scherer, N. F.; Shepanski, J. F.; Zewail, A. H. Picosecond Pump–Probe and Polarization Techniques in Supersonic Molecular Beams: Measurement of Ultrafast Vibrational-Rotational Dephasing and Coherence. *J. Chem. Phys.* **1984,** *81,* 2181–2182; Scherer, N. F.; Perry, J. W.; Doany, F. E.; Zewail, A. H. Ultrafast Molecular Relaxation of Isolated Stilbene: Measurements by Picosecond Pump-Probe Techniques. *J. Phys. Chem.* **1985,** *89,* 894–896.
84. Knee, J. L.; Doany, F. E.; Zewail, A. H. Intramolecular Dephasing in Pyrazine: Direct Picosecond Time Resolution. *J. Chem. Phys.* **1985,** *82,* 1042–1043; Knee, J. L.; Khundkar, L. R.; Zewail, A. H. Picosecond Mass-Spectrometry of a Collisionless Photodissociation Reaction. *J. Chem. Phys.* **1985,** *82,* 4715–4716; Knee, J. L.; Khundkar, L. R.; Zewail, A. H. Picosecond Monitoring of a Chemical Reaction in Molecular Beams: Photofragmentation of R–I → R‡ + I. *J. Chem. Phys.* **1985,** *83,* 1996–1998; IVR in Isolated

Molecules with Nearby Electronic States. *J. Phys. Chem.* **1985,** *89,* 3201–3202.

85. Lewin, R. A New Window Onto the Chemists' Big Bang. *Science* **1987**, *238* (Dec 11), 1512–1513.
86. Zewail, A. H. The Birth of Molecules. *Scientific American* **1990,** *263* (6), 76–82.
87. Baskin, J. S.; Zewail, A. H. Freezing Atoms in Motion: Principles of Femtochemistry and Demonstrations by Laser Stroboscopy. *J. Chem. Educ.* **2001,** *78,* 737–751.
88. Zewail, A. H. Transient Species at Femtosecond Resolution. Proc. Robert A. Welch Foundation, 38th Conf. on Chem. Res., Chemical Dynamics of Transient Species, Oct. 24–25, 1994, Houston, TX, 129–155.
89. Scherer, N. F.; Knee, J. L.; Smith, D. D.; Zewail, A. H. Femtosecond Photofragment Spectroscopy: The Reaction ICN → CN + I. *J. Phys. Chem.* **1985,** *89,* 5141–5143.
90. Kauffman, G. B.; Kauffman, L. M. Quantum Chemistry Comes of Age. *Chem. Educator* [Online] **1999,** *4* (6). 259–267; DOI 10.1007/s00897990333a; The Triumph of Quantum Chemistry. *Today's Chemist at Work* **1999,** *8* (10), 83, 85, 87.
91. Dantus, M.; Rosker, M. J.; Zewail, A. H. Real-Time Femtosecond Probing of "Transition States" in Chemical Reactions. *J. Chem. Phys*. **1987,** *87,* 2395–2397.
92. El-Sayed, M. A.; Tanaka, I.; Molin, Y. *Ultrafast Processes in Chemistry and Photobiology;* Blackwell Publishers: Cambridge, MA, 1995.
93. Pedersen, S.; Herek, J. L.; Zewail, A. H. The Validity of the Diradical Hypothesis: Direct Femtosecond Studies of the Transition-State Structures. *Science* **1994,** *266,* 1359–1364.
94. Rose, T. S.; Rosker, M. J.; Zewail, A. H. Femtosecond Real-Time Probing of Reactions. IV. The Reactions of Alkali Halides. *J. Chem. Phys*. **1989,** *91,* 7415–7436.
95. Scherer, N. F.; Khundkar, L. R.; Bernstein, R. B.; Zewail, A. H. Real-Time Picosecond of the Collision Complex in a Bimolecular Reaction: The Birth of OH from H + CO_2. *J. Chem. Phys.* **1987,** *87,* 1451–1453; Scherer, N. F.; Sipes, C.; Bernstein, R. B.; Zewail, A. H. Real-Time Clocking of Biomolecular Reactions: Application to H + CO_2. *J. Chem. Phys.* **1990,** *92,* 5239–5259.
96. Khundhar, L. R.; Zewail, A. H. Picosecond Photofragment Spectroscopy. IV. Dynamics of Consecutive Bond Breakage in the Reaction $C_2F_4I_2 \rightarrow C_2F_4 + 2I$. *J. Chem. Phys.* **1990,** *92,* 231–242.
97. Chang, P. Y.; Zhong, D.; Zewail, A. H. Transition States of Charge-Transfer Reactions: Femtosecond Dynamics and the Concept of Harpooning in the Bimolecular Reaction of Benzene with Iodine. *J. Chem. Phys.* **1995,** *103,* 5153–5156; Microscopic Solvation and Femtochemistry of Charge-Transfer Reactions: The Problem of Benzene(s)-Iodine Binary Complexes and their Solvent Structures. *Chem. Phys. Lett.* **1995,** *242,* 369–379; Su, J. T.; Zewail, A. H. Solvation Ultrafast Dynamics of Reactions. 14. Molecular Dynamics and *Ab Initio* Studies of Charge-Transfer Reactions of Iodine in Benzene Clusters. *J. Phys. Chem.* **1998,** *102,* 4082–4099.
98. De Feyter, S.; Diau, E. W.-G.; Scala, A. A.; Zewail, A. H. Femtosecond Dynamics of Diradicals: Transition States, Entropic Configurations and Stereochemistry. *Chem. Phys. Lett.* **1999,** *303,* 249–260; Diau, E. W.-G.; De Feyter, S.; Zewail, A. H. Femtosecond Dynamics of Retro Diels–Alder Reactions: The Concept of Concertedness. *Chem. Phys. Lett.* **1999,** *304,* 134–144; De Feyter, S.; Diau, E. W.-G.; Zewail, A. H. Femtosecond Dynamics of Norrish Type-II Reactions: Nonconcerted Hydrogen-Transfer and Diradical Intermediacy. *Angew. Chem., Int. Ed., Engl.* **2000,** *39*, 260–263; De Feyter, S.; Diau, E. W.-G.; Zewail, A. H. Femtosecond Dynamics of Norrish Type-II Reactions: Femtosecond Dynamics of Hydrogen Elimination: Benzene Formation from Cyclohexadiene. *Phys. Chem. Chem. Phys. (Roger Grice Special Issue)* **2000,** *2,* 877–883; Diau, E. W.-G.; Casanova, J.; Roberts, J. D.; Zewail, A. H. Femtosecond Observation of Benzyne Intermediates in a Molecular Beam: Bergman Rearrangement in the Isolated Molecule. *Proc., Nat. Acad. Sci.* **2000,** *97,* 1376–1379.
99. Syage, J. A.; Felker, P. M.; Zewail, A. H. Picosecond Dynamics and Photoisomerization of Stilbene in Supersonic Beams. I. Spectra and Mode Assignments. *J. Chem. Phys.* **1984,** *81,* 4685–4705; Syage, J. A.; Felker, P. M.; Zewail, A. H. II. Reaction Rates and Potential Energy Surface. *J. Chem. Phys.* **1984,** *81,* 4706–4723; Heikal, A. A.; Chong, S. H.; Baskin, J. S.; Zewail, A. H. Microscopic Friction and Solvation in Barrier Crossing: Isomerization of Stilbene in Size-Selected Hexane Clusters. *Chem. Phys. Lett.* **1995,** *242,* 380–389; Baskin, J. S.; Bañaras, L.; Pedersen, S.; Zewail, A. H. Femtosecond Real-Time Probing of Reactions: XX. Dynamics of Twisting, Alignment, and IVR in the *trans*-Stilbene Isomerization Reaction. *J. Phys. Chem.* **1996,** *100* (R. M. Hochstrasser Special Issue), 11920–11933; Heikal, A. A.; Baskin, J. S.; Bañaras, L.; Zewail, A. H. Structural Effect on the Isomerization Dynamics of *trans*-Stilbenes: IVR, Microcanonical Reaction Rates, and the Nature of the Transition State. *J. Phys. Chem.* **1997**, *101*, 572–590; Pedersen, S.; Bañaras, L.; Zewail, A. H. Femtosecond Vibrational Transition-State Dynamics in a Chemical Reaction. *J. Chem. Phys.* **1992,** *97,* 8801–8804.
100. Zewail, A. H. Laser Selective Chemistry—A New Challenge for Chemists and Physicists. *Engineering & Science (California Institute of Technology)* **1980,** *43,* 8–13.
101. Williamson, J. C.; Cao, J.; Ihee, H.; Zewail, A. H. Clocking Transient Chemical Changes by Ultrafast Electron Diffraction. *Nature* **1997,** *386,* 159–162; Ihee, H.; Cao, J.; Zewail, A. H. Ultrafast Electron Diffraction. Structures in Dissociation Dynamics of $Fe(CO)_5$. *Chem. Phys. Lett.* **1997,** *281,* 10–19; Ultrafast Electron Diffraction. Structures of Transient $Fe(CO)_4$: Determination of Molecular Structure and Reaction Pathway. *Angew. Chem., Int. Ed. Engl.* **2001,** *40,* 1532–1536; Cao, J.; Ihee, H.; Zewail, A. H. Ultrafast Electron Diffraction: Determination of Radical Structure with Picosecond Time Resolution. *Angew. Chem., Int. Ed. Engl.* **1998,** *290,* 1–8; Ultrafast Electron Diffraction and Direct Observation of Transient Structures in a Chemical Reaction. *Proc. Nat. Acad. Sci.* **1999,** *96,* 338–342; Ihee, H.; Lobastov, V.; Gomez, U.; Goodson, B.; Srinivasan, R.; Ruan, C.-Y.; Zewail, A. H. Direct Imaging of Transient Molecular Structures with Ultrafast Diffraction. *Science* **2001,** *291,* 458–462.
102. Reid, D. T. Toward Attosecond Pulses. *Science* **2001,** *291,* 1911, 1913; Drescher, M.; Hentschel, M.; Kienberger, R.; Tempea, G.; Spielmann, C.; Reider, G. A.; Corkum, P. B.; Krausz, F. X-Ray Pulses Approaching the Attosecond Frontier. *Science* **2001,** *291,* 1923–1927.
103. Zewail, A. H. Femtosecond Transition-State Dynamics. Structure and Dynamics of Reactive Transition States, Faraday Discuss. Chem. Soc. **1991,** 91, 207–237.
104. Hentschl, M.; Kienberger, R.; Spielmann, C.; Reider, G. A.; Milosevic, N.; Brabec, T.; Corkum, P.; Heinzmann, U.; Drescher, M.; Krausz, F. Attosecond Metrology. *Nature* **2001,** *414,* 509–513.
105. Jacoby, M. Laser Science: Attosecond Light Pulses Displayed: Extremely short bursts of light probe ultrafast electronic processes. *Chem. Eng. News* **2001,** *79* (49), 11.
106. Glanz, J. Which way to the Big Bang? *Science* **1999,** *284,* 1448–1451; Clark, S. *Towards the Edge of the Universe,* 2nd ed.; Springer-Verlag: New York, 1999.
107. Wilson, E. New Tool to Take Molecular Movies: Ultrafast electron diffraction finds new path for excited pyridine decay. *Chem. Eng. News* **2001**, *79* (52) (Dec. 24), 10.
108. Lobastov, V.; Srinivasan, R.; Goodson, B. M.; Ruan, C.-Y.; Feenstra, J. S.; Zewail, A. H. Ultrafast Diffraction of Transient Molecular Species in Radiationless Transitions. *J. Phys. Chem. A* **2001**, *105*, 11159–11164.

© 2002 Springer-Verlag New York, Inc., S1430-4171(02)02534-6, Published on Web 03/15/2002, 10.1007/s00897020534a, 720100gk.pdf