

Photochemistry and Photobiology

Edited by
Ahmed H. Zewail

Volume I
Laser Chemistry Applications



Proceedings of the International Conference,
University of Alexandria, Egypt, January 5-10, 1983

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Ahmed H. Zewail
California Institute of Technology



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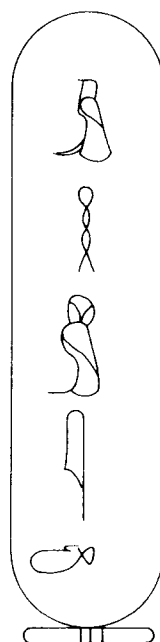
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To the people of Egypt, the land of the Pharaohs



Acknowledgments

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Foreword

Two thousand years ago Alexandria was the intellectual capital and the ancestor of a civilization which is now often designated by the word "Western." The fruits of Egyptian, Greco-Roman and other cultures were deposited in a library which was the most encompassing in its time. Unfortunately, the library was lost in a great fire. The harbor entrance of Alexandria was marked by a lighthouse of about the same height as the pyramids, and designated as one of the wonders of the ancient world. In the first century Hero of Alexandria recorded a basic law of optics, that the angle of incidence equals the angle of reflection from a plane mirror, and that the path of the light ray is faster than other geometric pathways in its vicinity. This is perhaps the first formulation of an extremum principle.

With the spread of Moslem religion, Arabic cultural elements dominated Alexandria. Important contributions to mathematics and chemistry were added, including the introduction of Arabic numerals. A fleet of crusaders used the port of Alexandria and the city was ravaged in numerous conflicts through the centuries. The moisture of the Mediterranean also contributed to the fact that little is preserved of the ancient glories of the city, in sharp contrast to the historic monuments elsewhere along the Nile.

Against this background Alexandria was a fitting locale to host a truly international conference on photochemistry and photobiology. A good deal of photophysics was also presented, as witnessed by the Proceedings in this volume. The conference provided for an intense interaction, both scientifically and socially, between attending biologists, chemists and physicists and their companions. They came from the East and the West, from Egypt's neighbors, Israel and Sudan, as well as from distant countries, on four different continents.

The conference room in the new building of UNARC, the Research Center of the University of Alexandria, provided comfortable seating, so that the participants could survive the demanding and lengthy sessions. They were further sustained by a series of meals, fine dinners, banquets, excursions and receptions which provided good

opportunities to strengthen old international ties and forge new ones. Our Egypt hosts may look back on the venture as worthy of the ancient tradition of Alexandria. All participants are grateful for this experience and express their gratitude for the Egyptian hospitality.

The conference was conceived, organized in its many details and concluded in these Proceedings by the special efforts of one individual. To him go our thanks from beginning to end, from A to Z, from Ahmed to Zewail.

NICOLAAS BLOEMBERGEN
Harvard University

Preface

The International Conference on Photochemistry and Photobiology (ICPAP) was held at the University of Alexandria Research Center (UNARC) on January 5–10, 1983. These volumes include more than one hundred papers presented by participants from fourteen nations. The topics of the conference varied, but focus was on the state-of-the-art in the fields of lasers, photochemistry and photobiology. The keynote addresses of the conference were given by the two Nobel Laureates: Sir George Porter, Director and Fullerian Professor of Chemistry, The Royal Institution, London, and Professor Nicolaas Bloembergen, Gerhard Gade University Professor, Department of Physics, Harvard University, Cambridge, Massachusetts.

There were perhaps two unique features of this conference. First, it drew together a very impressive number of prominent scientists from different areas of lasers, photochemistry and photobiology. Thus, interdisciplinary information from chemistry/physics/biology could be exchanged, yet focus on the major issues of the conference was still there. It was indeed gratifying to see the cross fertilization between fields as reflected in the almost complete attendance at all sessions. Second, several important papers were given as overviews which allowed these contributors to present the "latest work" on theories or experiments in their fields. Examples include overviews of non-linear optics and laser spectroscopy, photochemical energy storage, the picosecond-femtosecond developments, supersonic beams, energy redistribution in molecules, synchrotron radiation, and magnetic and optical interactions in biological systems. The crosslinking between these different aspects of lasers, photochemistry and photobiology and the gathering of outstanding scientists from all over the world ensured the success of the conference and led to the important contributions in these volumes.

The organization of this conference, conducted in the United States and Egypt, took more than a year, and a great many people helped, contributed, and encouraged me to continue at times when I felt it was impossible—I wish to thank them all! As only a few can

be mentioned here, I apologize in advance for my inability to list all of those who helped in this difficult but rewarding endeavor. In particular, I wish to sincerely thank my secretary, Mrs. Tina Wood, for her untiring work and dedicated efforts. Without Tina this task would have been impossible. I also thank the Egyptian trio—Laila, Nadia, and Mervat—for their enthusiastic efforts in the organization of this conference and the unselfish gift of their time. I also wish to acknowledge the genuine efforts of Dr. Sherif Kandil to ensure the success of the conference, and Dr. S. Farid for providing the hieroglyphic script—"changes with rays of light."

Several Caltech colleagues, members of the organizing committee and members of my research group have helped during the organization of this conference and in the final stages of assembling these proceedings. I am grateful to them for being generous with their time and efforts. Special thanks go to Mostafa El-Sayed, Rudy Marcus, Robin M. Hochstrasser, Vincent McKoy, Jean-Claude Lehmann, Jacques Joussot-Dubien, Hans C. Wolf and Ed Schlag. Thanks are also given to members of the local organizing committee (Egypt) who worked tirelessly to make the conference a success, both scientifically and socially. Finally, on behalf of the spouses of the participants I wish to thank most sincerely the local ladies program committee for their very warm and generous hospitality.

Last, but certainly not least, it is a pleasure to thank Professor Dr. M. El-Hadary, president of the University of Alexandria, Professor Dr. A. R. El-Sadr, director of UNARC, and Professor S. Morsi, Chairman of the local organizing committee; without their enthusiastic support we would not have had the ICPAP!

AHMED H. ZEWAIL
Pasadena, California

Chairman's Introductory Remarks

Ladies and Gentlemen,

My Colleague, Professor Salah E. Morsi, Chairman of the Local Organizing Committee, and I would like to welcome all of you to Alexandria and to Egypt. We are delighted that such a distinguished group of scientists in the fields of lasers, photochemistry and photobiology can be gathered here. I personally would like to thank all of my friends and colleagues from all over the world who helped, contributed and provided support throughout the organization of the conference, which took more than a year. We have a rich program, rich in its contents and rich because we are fortunate to have such outstanding participants from fourteen nations. We can all be assured that we will have many hours and days of hard work and exciting contributions!

Before I say a few more words about the conference, I would like to introduce our Egyptian hosts who will be welcoming you after these remarks: the President of the university, Professor Mahmoud El-Hadary, who will also present the greetings of the Deputy Prime Minister and Minister of Education and Scientific Research, Professor Moustafa Kamal Hilmy, who could not be here today; the Director of UNARC, Dr. A. R. El-Sadr; and the Governor of Alexandria, General Mohamed Fawzi Maaz.

It is not accidental that Egypt hosts such an outstanding and International Conference on Photochemistry and Photobiology for many reasons. First, during the Egyptian ancient civilization, several thousands of years ago, Alexandria was the home of the first known research institution and the very famous library; scientists and scholars from all over the world came to Alexandria to gather and to learn about the scientific truth—it was through this institute that discoveries were made, among them the proof that “THE EARTH IS ROUND.” Euclid and other notable scientists were Alexandrians.

Second, one of the first breakages of molecules by light—photochemistry—was done here by Egyptian scientists using Egypt's Giza (or Abbassia) solar radiation. The school of the late pioneer Professor Ahmed Mustafa† is well known internationally and his book on the subject is a classic. His work with Professor Schönberg done here in Egypt led to new discoveries in photochemistry and photomedicine—among these is the famous Schönberg–Mustafa reaction published in 1944 about photoinduced (4+2)-cycloaddition of *o*-quinones to olefinic double bonds. Using, and even worshipping, the Sun is a very ancient Egyptian tradition.

Third, Egypt is now reviving its ancient scientific tradition in basic and applied research in Alexandria by establishing one of the most promising institutions—UNARC. One of the main purposes of the conference is to initiate “interactions” between Egyptian scientists and leading worldwide scientists. Through interactions and presentations new directions can be initiated at UNARC and in Egypt, and these leading scientists will learn more about UNARC and Egypt's science and technology.

Finally, the fourth reason is personal and perhaps selfish. I graduated from this university, and it gives me great and special pleasure to be part of this conference. Actually, two of the people *responsible for my “exile”* are present—Professor El-Sadr, who signed my papers for the study leave (he was at that time the Vice President of the university) and Professor Robin Hochstrasser, who received me as a graduate student in the United States. Professor Hochstrasser was and still is a professor at the University of Pennsylvania.

This concludes our opening ceremony. We are looking forward to opening our scientific session this afternoon with keynote addresses by the Nobel Laureates, Sir George Porter of the Royal Institution and Professor Nicolaas Bloembergen of Harvard University.

AHMED H. ZEWAIL

† Note that Mustafa (or Mostafa) El-Sayed and I are “by-products” of Professor Ahmed Mustafa: Ahmed Zewail + Mustafa El-Sayed = Ahmed Mustafa + Zewail El-Sayed; where is Zewail El-Sayed?—not known, perhaps in the tombs of the Pyramids.

Director's opening address

Alexandria—Its Naissance and Renaissance

Distinguished Guests, Excellencies, Dear Colleagues,

According to tradition, my talk should start by a welcoming statement and an expression about how much it is a privilege and an honour to address such a distinguished audience. I think I shall have to drop all that because it is a fact that you already know and feel. But also because of two other pressing forces: first, my treating cardiologists have advised me to limit my talk to not more than 30 minutes, and second, because our chairman, Professor Zewail, has allotted only 20 minutes—at most 23—for this talk. Since I am presenting “Alexandria—its Naissance and Renaissance” which covers a period of 23 centuries, Professor Zewail is allowing me 23 minutes. Accordingly, I am dropping my welcoming remarks, and I depend upon your wisdom in understanding my difficulty and in granting me an excuse. This action on the part of Zewail, however, is welcome since it immediately puts into focus one principle of UNARC's policy, which I will refer to later. This principle is “Authority and Seniority are not necessarily compatible”—a rule contrary to the prevailing concept in our society.

Getting back to our subject, I believe being in Alexandria is an event of special flavor to any scientist. Realizing that one is stepping on the very land where Alexander the Great once stepped, that he himself chose the place for us to gather today, that one is finally in the city that was the first center for knowledge and learning, where the great museum was erected and the great library was first established, where the largest number of manuscripts of the time were first collected, where the *Pharos* once magnificently stood as one of the seven wonders of the world, all this can make the event a great sensation, and makes Alexandria a real Mecca for individuals in love with science.

As a matter of fact, writers who visited Alexandria during the present century, and who have had the time and drive to imbibe its

history in depth and breath, fell in love with the city and wrote passionately about it. Of those, E. M. Forster, who lived here during the first world war as a Red Cross volunteer, wrote his book: *Alexandria, History and a Guide*, in which he expressed his love for this unique social, scientific and spiritual city. The book was first published in Alexandria, 1922, and again, 1938, in New York, 1961, and lately in London, 1982. He referred to his friend C. P. Cavafy, the great Greek poet who so poignantly conveys the civilization of his chosen city.

Laurence Durrell, who stayed in Alexandria during the second world war, became so enchanted by the city that he was inspired to write his famous "Alexandria Quartet" that captured world wide admiration.

Lately, a young scientist, Carl Sagan, joined those writers when he wrote so devotedly about the old city and its great library, referring to the achievements that took place in it and in its museum, pointing out in his book *Cosmos* published in New York, 1980, how Alexandria was not only the geographical center of the then known world, but also the center of gravity of scientific life in this world.

In his great drive towards the east to conquer Persia, and at the age of 25, Alexander of Macedonia, after paving his way through Asia Minor and Assyria, arrived in Egypt by land in 331 BC. When arriving and studying the Mediterranean coast, he ordered his architect Dinocrates to plan and construct a magnificent Greek city on a spot at arm's length from the spot where we now gather. He had no time to wait and hurried on, and he never saw a single building rise in the city that bore his name. After his death in Babylon, Egypt became the lot of his senior general, Ptolemy, who occupied himself with the creation of the city and putting life into it. The dynasty ruled for three centuries, to be followed by gradual but progressive decline with the Roman conquest.

The main landmarks of Alexandria then were: *The Pharos*, that stood 400 feet high to guide ships towards the flat shore of Egypt; *The Palace*, residence of kings and site of government; *The Museum*, physically and spiritually connected with the palace and thus very subject to the advantages and disadvantages of royal patronage. In some ways, it resembled a modern university, but the scholars, scientists and library staff were under no obligation to teach. Their main occupation was to follow their studies for the greater glory of the Ptolemies.

The most important element of this institution was the Library, sometimes called the "mother library" to distinguish it from a later and even greater collection, that was housed in and near The Temple of Serapis, a god invented by the Ptolemies that acquired both Greek and Egyptian features to consolidate the bond of the two societies; it did work well.

Other buildings were erected, roads constructed, colonnades built, palaces, baths, markets, theaters, a race course, and tombs formulated the new city. It soon became the center of commerce, culture and learning. The population comprised Egyptians, Greeks, Armenians, Phoenicians, Africans, Assyrians and Hebrews. This variety composed the first cosmopolitan city in the world. They lived together a joyous and harmonious life in great splendor, enjoyed art and pleasure, practiced trade and travel; in short, it was a truly affluent society. In this background science thrived.

However, philosophy did not flourish in Alexandria since the kings thought it might lead to freedom of thought whereas science could not criticize their divine rights. But Alexandrian philosophy arose to great heights at the hands of Christianity, and Alexandria took leadership in the religious issues that prevailed at the time.

The Ptolemies' endowment to science was the greatest achievement of the dynasty and it made Alexandria famous until the end of time. Geography, mathematics, astronomy, and medicine all grew to maturity and achieved levels of knowledge that still remain solid today. I do not intend to enumerate names of the many scientists who lived and worked here, but one might point out certain outstanding ones like Eratosthenes, once the librarian of the legendary Library, and a great geographer. Through a simple experiment performed at the borders of Egypt in the south, and at its Mediterranean shore in the north, here in Alexandria, using sticks and measuring angles, Eratosthenes was able to verify that the Earth was round and could measure, with minor error, its circumference and its radius. He stated that because the Atlantic Ocean was so vast, it became the only obstacle to circumnavigation of the Earth and to sailing from Iberia to India. Christopher Columbus, in his discovery of America, depended upon the work of Copernicus and Galileo, but also upon the calculations of Eratosthenes.

Other Alexandrians, among them Aristarchus of Samos, argued that Earth is a planet that orbits the sun like other planets. Apollonius of Perga, the mathematician, demonstrated the forms of conic

sections, and his writings were to be used 18 centuries later by Kepler in understanding for the first time the movements of the planets.

And what about Euclid, the great mathematician, the father and founder of geometry who concerned himself with the description of special relationships on a plane and who conceived so early what we now call deductive framework? Heron, inventor of gear trains and steam engines, the author of *Automata*, the first book on robots. Archimedes, the greatest mechanical genius until Leonardo da Vinci, invented the water screw, which has remained in use by Egyptian farmers to this day for raising water, and land irrigation, though he thought then that his invention was below the dignity of science.

In medicine, Herophyles stands high. He dissected the human corpse in his studies, which was prohibited in Greece. He realized fantastic conclusions which hold quite well today. He concluded that the brain rather than the heart was the center of intelligence, the concept held by Aristotle. He identified nerves, arteries and veins, stated that nerves were responsible for sensation and movement, that blood flows from veins to arteries through very fine channels, the first concept of circulation, although in the reverse direction.

The calendar we are now using originated in Egypt, was rectified in Alexandria and modified by Julius Caesar.

Now the question presents itself: did all this great advancement in Alexandria evolve from Greek origin? In ancient Greece, science was sporadic, yet philosophy and literature were alive. In Ptolemaic Alexandria, philosophy was nil, whereas science was overwhelmingly active. There seems no doubt that Greek thought over Egyptian soil led to an outstanding development. In this context, it may suffice to refer to facts extracted from scholarly studies performed about the Great Pyramid, and the genius of its builders. The measurements that were adhered to, the angles that were applied, and height that was attained indicated inconceivable greatness, as was cited by so many scholars.

Peter Tompkins wrote a book, that either has been published or will be very soon, whose title is *The Secrets of the Great Pyramid*. In his book, Tompkins recites fantastic data that resulted from studies and observations which spread over 10 centuries, from the time of Al-Maamoon, Caliphate of the 10th century, up until the 20th century, when the Egyptian government hired J. H. Cole in 1924 to do the most precise measurements of the Pyramid, as a professional

surveyor. Tompkins reached thrilling conclusions summarized from these studies that I quote here: he says:

It is now clear that the Great Pyramid is both a scale model of the Northern Hemisphere and an astronomical observatory, and that the men who designed it were sufficiently versed in astronomy, mathematics and geography to have known that the world was round, to calculate its circumference and polar axis, and to have been aware that it rotates once a day around an axis tilted about $23\frac{1}{2}$ degrees, and revolves around the sun once in a year of 365 and a fraction days. The designers must also have known that the constellations of heavens appear to slip backwards approximately every 2200 years in a grand cycle of about 26 000 years.

Strichinni, a scholar from Harvard and a specialist in ancient measurements, demonstrated that Eratosthenes did not establish the circumference of the earth as he is currently fabled to have done by measuring the zenith distance at Alexandria at the summer solstice when the sun cast no shadow in a well at the tropical border of Egypt at Syene. He says: "Eratosthenes, as the chief of the Library of Alexandria, simply picked up fragmented data that had been correct 2000 years earlier, as demonstrated by studies conducted on the Great Pyramid of Giza."

I would not go that far since the experiments of Eratosthenes are different from and quite separable from the concepts perceived in the erection of the Great Pyramid. Yet one may point out that such a statement indicates that contacts between Greek and Egyptian cultures were fairly extensive and that the twining of the two could have been a real factor in the development of science in Alexandria. Thus the boats of Columbus, which in fact sailed from Iberia, may not have started their journey in theory at Alexandria, but they even might have started it in Giza, at a site next to the sun boats of the Great Pyramid.

One momentous event in the history of the decline of Alexandria is the myth about the fire that destroyed its fabulous library. During my travels, being Alexandrian, I was repeatedly questioned about the fate of that library. Without exception, everyone had the information that it was the Arabs who put the library to fire.

It was Bar Hebrus, who in his book *The History of Nations* first propagated the story, that originated with him, that the Arabs, after the conquest of Egypt, were responsible for deliberately committing the Library of Alexandria to fire. This rumor was communicated,

parrotlike, from writer to writer and from age to age. In the last century, however, some brilliant historians, Gibbon and Butler among them, began to investigate the tradition. In the light of technical scholarship and historical evidence, they were able to present historical facts to the contrary. It is not in the order of logic that these devout Arabs, who subsequently and within the space of 50 years, were able to inspire the world with their quest for knowledge and piety for learning, and who on several instances were persistent in their claims to secure all the manuscripts and books, as a condition for peace, in wars with their adversaries, would commit such a fine library of its time to fire, and to use its documents to heat their bathrooms, as was claimed. It is inconceivable, on the other hand, that these missionaries of the desert had the time to settle and to develop the habit of bathing in heated bathrooms.

In Islam the quest for knowledge attains prime importance. To be sure, the first passage of the holy Koran that was addressed to the then illiterate prophet reads "Read in the name of your God, who initiated the creation." Many other passages induce Moslems to pursue learning and to acquire knowledge.

Late scholarly studies indicate that the fire did really take place, but during the 4th century AD, in the course of a national uprising led by the monks of Christianity against paganism that still existed and was symbolized by the museum and its dwellers. The Arabs arrived in the 7th century, 643 AD. The Library had already disappeared 300 years earlier. In fact, if the Library were still here, Alexandria would have become most probably the capital of Egypt under the Arabs. That was not the case, and the loss of the Library resulted in the deterioration of Alexandria for almost 1000 years. It is significant that the University of Alexandria is presently concerned with establishing a great library with up-to-date facilities and services that would occupy the east wing of this very same building. UNARC and its library would commemorate the ancient library and in a way establish a replica of the old museum and its library.

The rebirth of Alexandria started at the very end of the 18th century, and took course all through the 19th century. My personal conviction is that renaissance of Alexandria was triggered by the arrival of Napoleon Bonaparte at its shore in 1798. He organized a most extraordinary expedition to Egypt, accompanied by an intellectual task force of 175 scholars, not to conquer, but rather to discover