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

Thesis by

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Dedicated with love and gratitude

to

Bhagawan Sri Sathya Sai Baba

and to

my dearest parents

Aruna and N.V. Srinivasan

Acknowledgements

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

she would say, 'did you ask a good question today?' That difference–asking good questions–made me become a scientist." It has been my singular fortune to learn from Prof. Zewail the art of asking the right questions. I have enjoyed our numerous discussions on the history of science, on the role of science and technology in bridging the gap between the 'haves' and the 'have-nots', on the cultural mores of our respective ancient civilizations, and on the art of communicating science to non-scientists and especially to young, budding scientists. While he has been a wonderful teacher, I hope I have been a worthy disciple. I am also grateful to his wife, Dema, and his sons, Hani and Nabeel, for giving me a home away from home, for many wonderful evenings of joy and laughter.

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Abstract

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

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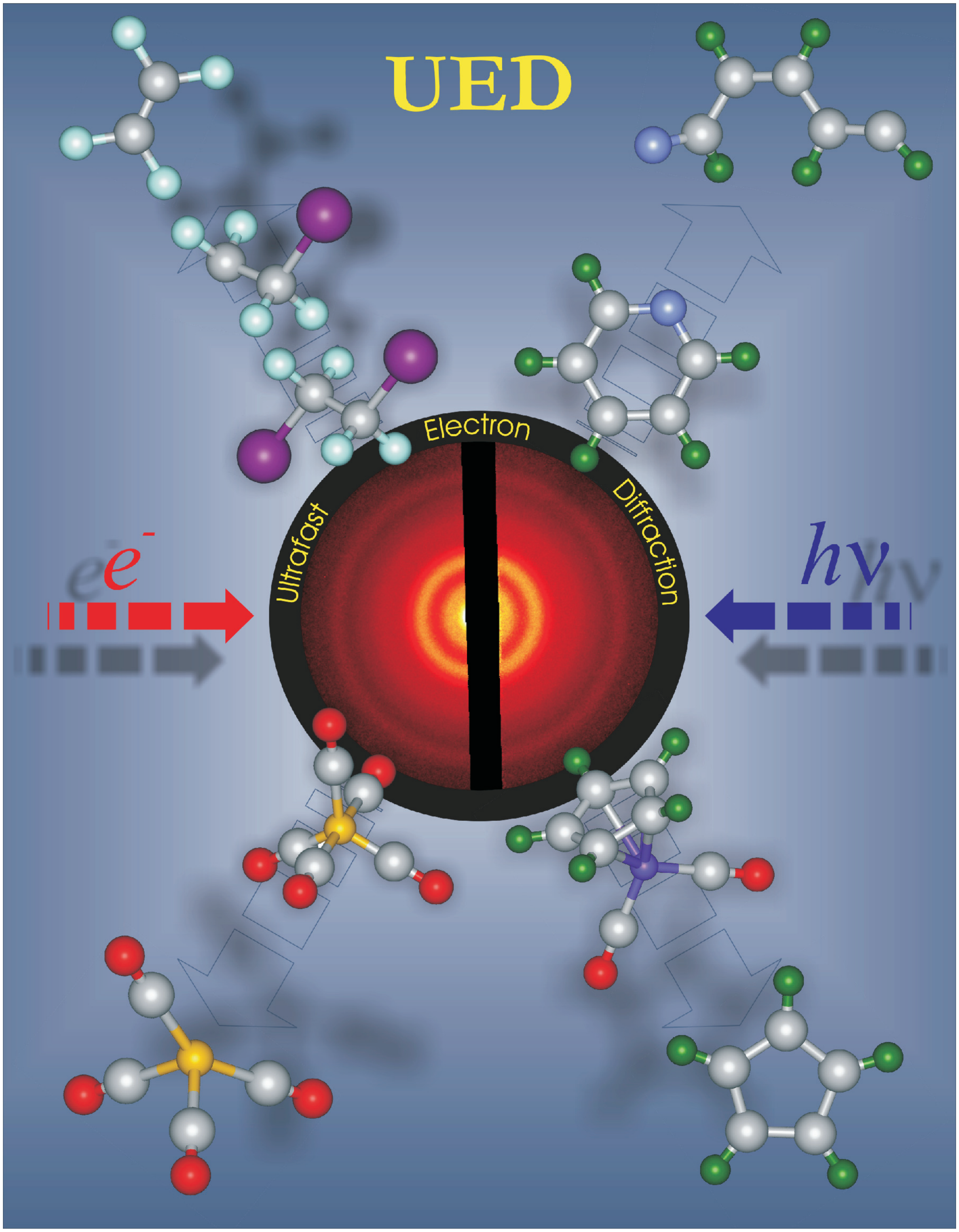
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Electron
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