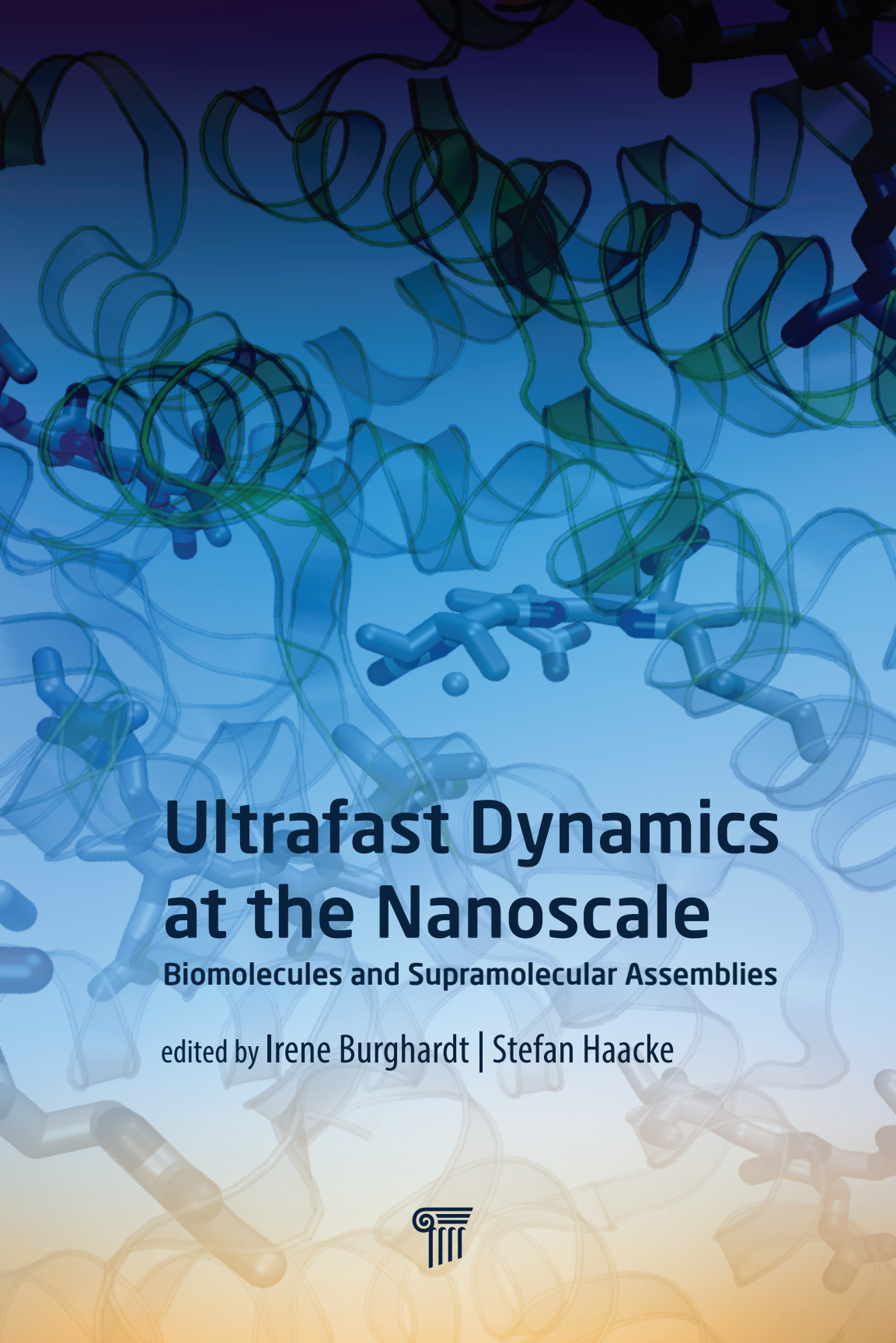

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Biomolecules and Supramolecular Assemblies

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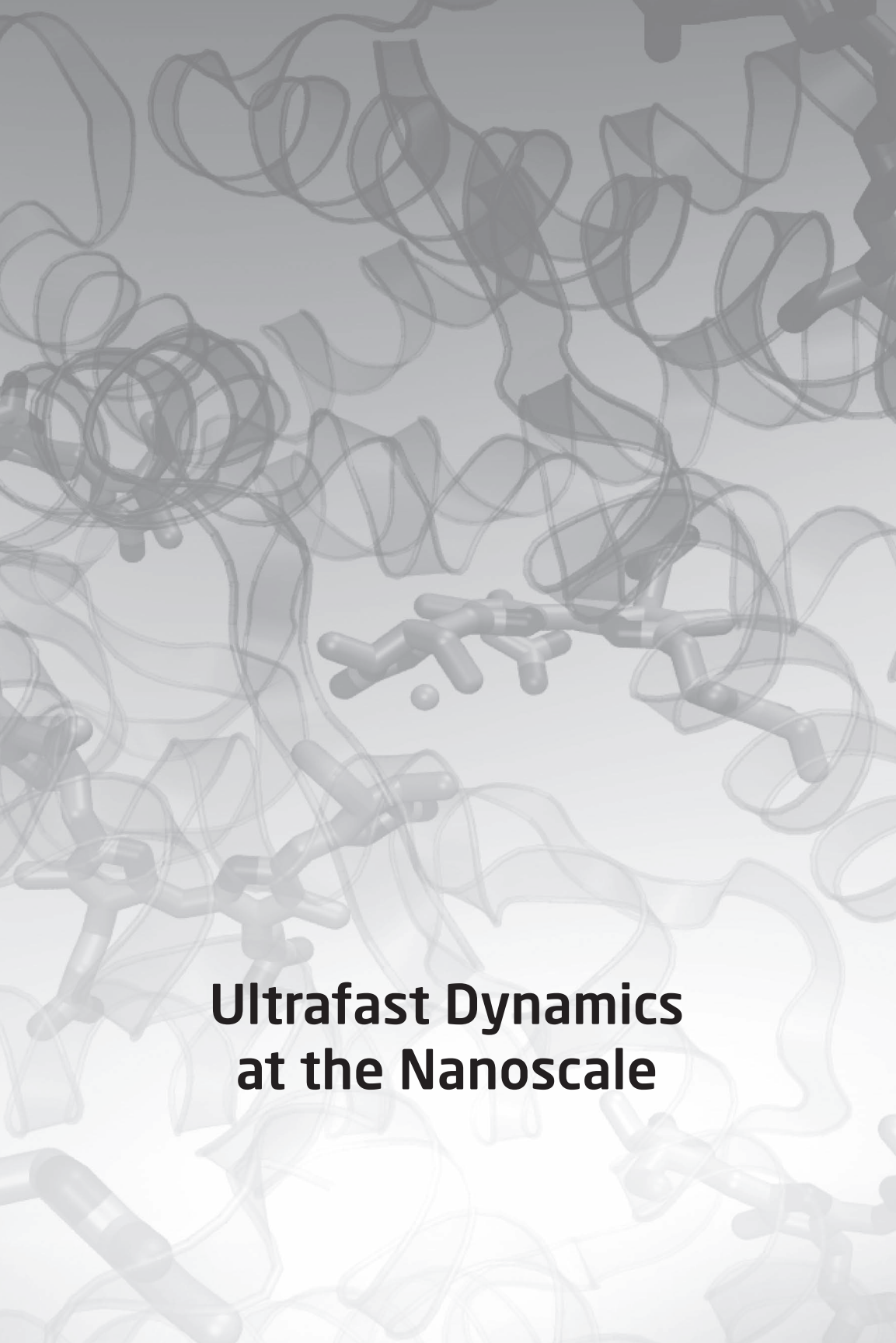

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Preface

Over the past decade, research on ultrafast (bio)molecular dynamics has evolved significantly, from spotlighting isolated molecular species toward focusing on molecular assemblies, including chromophore–protein complexes, biopolymers like DNA and RNA, and functionalized systems like combinations of biomolecules and inorganic nanoparticles, plasmonic nanostructures, and semiconducting polymer materials. Potential applications range from light harvesting to biosensing, artificial signal transduction, and organic photovoltaics. The functionality and control of these systems are currently under intense investigation in view of developing a detailed understanding of ultrafast nanoscale energy and charge transfer, as well as fostering novel technologies based on sustainable energy resources. At the same time, fundamental issues like the role of quantum coherence versus decoherence have moved into focus. The book aims to illustrate this evolution—which is far from complete at the time of publication—with contributions from top researchers in the field.

The book groups together 13 chapters, comprising 6 contributions from spectroscopy and 7 from theory and computation. Within a broad range of topics, from DNA photostability and repair to light-harvesting complexes and novel hybrid materials, a common denominator is the key importance of ultrafast quantum effects at the border between the molecular scale and the nanoscale. Contributions include cutting-edge developments in ultrafast nonlinear optical spectroscopies and quantum dynamical simulations of the observed dynamics, including direct simulations of two-dimensional optical experiments. Taken together, these techniques attempt to elucidate whether the quantum coherent nature of the ultrafast events persists in the presence of strong vibronic interactions and

electrostatic couplings to the environment. Moreover, it is still an open issue to date whether the coherent nature of the elementary events possibly enhances the efficiency of the relevant processes and where the quantum-classical boundary sets in in these highly complex biological and material systems.

The first experimental contribution, by B. Kohler (Chapter 1), offers a didactic introduction to the fundamental concepts of ultrafast transient absorption spectroscopy in the context of investigating isolated DNA bases or single-stranded DNA. This review emphasizes the recent progress in understanding how base stacking influences the excited-state electronic structure and modulates nonradiative processes such as exciton and charge transfer involving neighboring nucleic acid bases. These studies are also driven by the general interest in ultrafast nonradiative internal conversion processes, which are believed to protect DNA from photodamage by UV light.

Active photoinduced repair of DNA is carried out by photolyases, that is, photoreactive enzymes which were discovered more than 50 years ago. Two contributions in this book highlight the recent advances made in dissecting the molecular details and reaction steps of enzyme photoactivation, involving ultrafast intraprotein charge transfer processes, and repair of different types of lesions. K. Brettel, M. Byrdin, and M. Vos (Chapter 2) devised a special transient absorption experiment with high sensitivity dedicated to the investigation of how DNA photolyases repair so-called CPD lesions, involving forward and backward electron transfer between the photolyase enzyme and a defective covalently linked thymine pair site. D. Zhong and his collaborators (Chapter 3) report results for the same type of system and complete this topic by reviewing their present understanding of the electron and proton transfer processes between photolyase cofactors and the nucleobases involved in repair of mutagenic so-called 6-4PP lesions. Both studies demonstrate the power of ultrafast multiwavelength transient absorption spectroscopy in revealing reaction kinetics and quantum yields, but also the particular effort involving the investigation of many mutants and molecular variants—a tour de force that is required to identify the often overlapping spectral signatures of the multiple species involved in these complex photoreactions.

The photoactive yellow protein (PYP) is a prototypical photosensor protein used by some bacteria to avoid harmful UV light (negative phototactic response). M. Groot and K. Hellingwerf (Chapter 4) have worked out the intimate details of the primary photoreactions involving a subpicosecond photoisomerization of the *p*-coumaric acid chromophore, the covalently bound cofactor of PYP. Besides providing a review of the different complementary time-resolved spectroscopy and X-ray diffraction techniques, the authors' report on the investigation of point-mutated PYP provides critical information on how the protein environment tunes and controls the different kinetic steps in the PYP photocycle.

Inspired by the concept of light harvesting through distributed multichromophore absorption, I. Nabiev and his team (Chapter 5) have implemented new nanobio hybrid materials, where semiconductor quantum dots with highest extinction coefficients are covalently bound to bacteriorhodopsin or photosynthetic reaction centers. The process of Förster resonant energy transfer (FRET) was studied in detail for these novel donor–acceptor systems, along with the key question of how the functional efficiency of these hybrids is enhanced as compared to the bare proteins. This work exemplifies an important emerging research direction aimed at exploiting the synergy of biomolecules and synthetic nanostructures in hybrid materials for improved photon harvesting and energy conversion.

In the final experimental chapter, A. Cannizzo et al. (Chapter 6) present different approaches to directly probe the spectroscopic response of the protein environment interacting and modulating the ultrafast photochemistry of the reactive cofactor. The authors summarize their work on using Trp residues as local reporters through intraprotein Stark effects or energy transfer. Two-dimensional femtosecond spectroscopy techniques are in principle the method of choice for the investigation of coupled multichromophoric systems. The present progress of their challenging implementation in the near-UV spectral region, targeting amino acids or nucleobases, is reviewed.

On the theory side, the Fenna–Matthews–Olson (FMO) complex, a pigment–protein complex appearing in green sulfur bacteria, has served as a paradigm system over recent years for studying

excitation energy transfer in biological light-harvesting systems. The chapters by P. Nalbach (Chapter 7) and P. Huo and D. Coker (Chapter 8) both address this system, using path integrals, master equation techniques, and novel mixed quantum-classical approaches to solve the highly non-Markovian, correlated quantum dynamics of this multichromophoric system. Key issues include the role of spatial and temporal correlations in inducing long-lived excitonic coherences and the relevance of these coherences for the efficiency of the light-harvesting process. While earlier contributions in this field were strongly suggestive of an enhanced quantum efficiency of biological light harvesting, the viewpoint by Nalbach, Huo, and Coker tends to be critical in this regard.

In the following contribution, S. Jang (Chapter 9) develops a quantum master equation in the polaron picture, which is able to interpolate between the coherent and incoherent regimes of excitation energy transfer in multichromophoric systems. Together with the approaches mentioned above, this work illustrates the importance of adapting existing quantum propagation techniques to the treatment of high-dimensional systems that do not allow for standard approximations like weak-coupling limits or separation of timescales. Instead, alternative zeroth-order pictures need to be found—as exemplified by the polaron transformation—that are able to capture the strong vibronic (electron–phonon) coupling effects that are ubiquitous in biological systems and organic materials.

The theoretical treatment of hybrid assemblies involving metal nanoparticles and single molecules or molecular assemblies is an important and challenging aspect accompanying recent experimental developments in this area (cf. Chapter 5 by I. Nabiev). Indeed, plasmonics—relating to the specific spectroscopic and transport properties of collective electronic excitations in noble metal nanoparticles—has become a rapidly emerging area within the field of nanotechnology, sensing, and biophotonics. Against this background, V. May and collaborators (Chapter 10) develop a consistent time-dependent quantum description, at a density matrix level, of resonant energy transfer involving multipole collective electronic excitations of the metal nanoparticle and molecular transitions of the acceptor system. This elegant approach naturally

connects to the class of master equation approaches mentioned above.

The contribution by H. Tamura et al. (Chapter 11) addresses photoinduced energy and charge transfer in organic photovoltaic materials, using a combination of electron–hole model Hamiltonians parametrized by electronic structure calculations, and high-dimensional quantum dynamics using efficient multiconfigurational methods. This approach offers an alternative to master equation and path integral strategies, attempts to build a maximum of molecular information into a first-principles parametrized model Hamiltonian, and systematically exploits the lattice structure of the relevant materials. As a result, a precise picture of highly nonexponential, non-Markovian transfer processes in composite donor–acceptor systems can be obtained, as exemplified by a study of the fullerene-based P3HT–PCBM paradigm system.

The final theory chapters by J. Yuen-Zhou, A. Aspuru-Gúzik and collaborators (Chapter 12) as well as A. Dijkstra and Y. Tanimura (Chapter 13) are concerned with the simulation of nonlinear optical spectroscopic experiments with a focus on multichromophoric assemblies. The interpretation of such experiments, which encode information on transport processes in spectral signatures (e.g., cross-peaks in two-dimensional spectroscopies) is often complex and critically relies on theoretical analysis. In this context, Yuen-Zhou et al. give a didactic introduction to pump–probe spectroscopy, connecting to a quantum information theory setting, while Dijkstra and Tanimura focus on two-dimensional spectra and explore the quantum-classical transition from the viewpoint of spectroscopic observables.

While being far from comprehensive, we believe that the present collection of contributions provides a combined experimental and theoretical spotlight on the molecular-level investigation of light-induced quantum processes in biological systems and nanostructured assemblies. We hope that this collection will inspire future experiment–theory connections at this frontier between molecular and nanoscale quantum phenomena.

We would like to express our sincere gratitude to the authors, colleagues, and friends who joined this book project with the

aspiration to present their research in a creative and pedagogical style. Finally, we are most grateful to the editorial team at Pan Stanford Publishing for its invaluable help with publishing this volume.

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Stefan Haacke
Frankfurt and Strasbourg, July 2016