



Ultrafast Dynamics at the Nanoscale

Biomolecules and Supramolecular Assemblies

edited by Irene Burghardt | Stefan Haacke



The background of the slide is a complex, overlapping arrangement of protein structures. These structures are rendered in a light gray, semi-transparent style, showing various folds, loops, and helices. The overall effect is a dense, textured field of molecular models. In the center of the slide, there is a single protein structure rendered in a darker, more solid gray, which stands out from the lighter background. This central structure appears to be a small, globular protein with several distinct domains.

**Ultrafast Dynamics
at the Nanoscale**

Ultrafast Dynamics at the Nanoscale

Biomolecules and Supramolecular Assemblies

edited by
Irene Burghardt
Stefan Haacke

PAN STANFORD  PUBLISHING

Published by

Pan Stanford Publishing Pte. Ltd.
Penthouse Level, Suntec Tower 3
8 Temasek Boulevard
Singapore 038988

Email: editorial@panstanford.com

Web: www.panstanford.com

British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library.

**Ultrafast Dynamics at the Nanoscale: Biomolecules and
Supramolecular Assemblies**

Copyright © 2017 Pan Stanford Publishing Pte. Ltd.

All rights reserved. This book, or parts thereof, may not be reproduced in any form or by any means, electronic or mechanical, including photocopying, recording or any information storage and retrieval system now known or to be invented, without written permission from the publisher.

For photocopying of material in this volume, please pay a copying fee through the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, USA. In this case permission to photocopy is not required from the publisher.

ISBN 978-981-4745-33-8 (Hardcover)

ISBN 978-981-4745-34-5 (eBook)

Printed in the USA

Contents

Preface xiii

SECTION I EXPERIMENT

1 Excited States of Single-Stranded DNA Revealed by Femtosecond Transient Absorption Spectroscopy	3
<i>Bern Kohler</i>	
1.1 Introduction	4
1.1.1 Origins	5
1.2 The TA Experiment	6
1.2.1 The TA Signal	8
1.2.2 Dispersive Pulse Broadening and Temporal Walk-off	11
1.3 Transient Absorption Signal Strength	14
1.3.1 Bleach Recovery Signals	18
1.3.2 DNA TA Experiments	19
1.4 Excited-State Dynamics of Single DNA Strands	22
1.4.1 Structure of $(dA)_n$ Single Strands	25
1.4.2 TA Signals from $(dA)_n$ Single Strands	30
1.4.3 Estimating Quantum Yields from Bleach Signals	34
1.4.4 Exciton Dynamics	41
1.5 Summary	43
2 Ultrafast Light-Induced Processes in DNA Photolyase and Its Substrate-Bound Complex	65
<i>Klaus Brettel, Martin Byrdin, and Marten H. Vos</i>	
2.1 Introduction	65

2.2	Energy Transfer	69
2.3	Photoactivation	70
2.4	Photorepair	75
3	Dynamics and Mechanisms of Ultraviolet-Damaged DNA	
	Repair by Photolyases	91
	<i>Zheyun Liu, Lijuan Wang, and Dongping Zhong</i>	
3.1	Introduction	92
3.2	Reaction Mechanism of CPD Repair by Photolyase	94
3.3	Reaction Mechanism of 6-4PP Repair by Photolyase	101
3.4	Electron-Tunneling Pathways in DNA Restoration	106
3.5	Concluding Remarks	117
4	Photoactive Yellow Protein: Converting Light into a Metastable Structural Change	127
	<i>Marie Louise Groot and Klaas J. Hellingwerf</i>	
4.1	Introduction	128
4.2	Ultrafast Experiments: How to ...?	131
4.3	Timescale and Mechanism of Isomerization	134
	4.3.1 Timescales	134
	4.3.2 Isomerization	136
	4.3.2.1 Excited state	137
	4.3.2.2 I_0 state	137
	4.3.2.3 I_1 state	139
	4.3.3 Mechanism	141
4.4	Role of Charges in the Protein Cavity	142
4.5	Role of Hydrogen Bonds to the Phenol Ring and the Carbonyl Group of the Chromophore	143
	4.5.1 Hydrogen Bonds to the Phenol Ring	143
	4.5.2 Hydrogen Bonds to the Carbonyl Group	146
4.6	Role of Water Molecules	147
4.7	Emerging Picture and Open Questions	148
4.8	Applications of PYP: General Aspects	150
4.9	Applications of PYP: Examples	152

5 Energy Transfer Mechanisms in Nanobiohybrid Structures Based on Quantum Dots and Photosensitive Membrane Proteins	167
<i>Svetlana V. Sizova, Vladimir A. Oleinikov, Nicolas Bouchonville, Michael Molinari, Pavel Samokhvalov, Alyona Sukhanova, and Igor Nabiev</i>	
5.1 Introduction	168
5.2 Possible Energy Transfer Mechanisms in Nanobiohybrid Structures Based on Photosensitive Biomolecules and Quantum Dots: Nonradiative and Radiative Energy Transfer	169
5.3 The Quantum Dot–Bacteriorhodopsin Nanobiohybrid Structure	176
5.3.1 Bacteriorhodopsin: Structure and Function	176
5.3.2 Energy Coupling between Quantum Dots and Bacteriorhodopsin in Aqueous Media	178
5.3.3 Methods of Forming Heterostructures Containing Quantum Dot–Bacteriorhodopsin Complexes	182
5.3.4 Quantum Dot–Bacteriorhodopsin Hybrids in Dried Films as Media for Sensing and Optical Applications	184
5.3.5 Enhancement of the Biological Functions of Bacteriorhodopsin by Means of Coupling with Quantum Dots	185
5.4 The Quantum Dot–Photosynthetic Reaction Center Nanobiohybrid Structure	189
5.4.1 Bacterial Photosynthetic Reaction Centers: Structure and Properties	189
5.4.2 Energy Transfer from Quantum Dots to Bacterial Reaction Centers	192
5.5 Conclusions and Perspectives	199
6 Ultrafast Functional Dynamics in Proteins: Local Molecular Reporters and Femtosecond 2D Spectroscopy	207
<i>Andrea Cannizzo, Jérémie Léonard, and Stefan Haacke</i>	
6.1 Introduction	208

6.2	Photoinduced Charge Translocation and Dynamic Dielectric Response	210
6.2.1	Ultrafast Response of Amino Acids: Example of Retinal Proteins	210
6.2.2	Photoinduced Charge Transfer and Dielectric Dynamics Probed by Transient Trp Absorption	214
6.3	Local Fluctuation and Energy Redistribution in Biomolecules	216
6.3.1	Solvation and Local Fluctuation	216
6.3.2	Dissipation and Redistribution of Energy in Hemoproteins	218
6.4	Tracking Down Concerted Motions in Proteins and Molecular Devices: An Outlook on Coherent UV Spectroscopies	226
6.4.1	UV Multidimensional Spectroscopies	226
6.4.2	Pulse Shaping and Automated UV 2D Spectrographs	233
6.4.3	All-Optical Chemically Sensitive Coherent Spectroscopies	236
6.5	Conclusions/Final Remarks	238

SECTION II THEORY

7	Ultrafast Exciton Dynamics in Correlated Environments	257
	<i>Peter Nalbach</i>	
7.1	Photosynthesis and Energy Transfer	257
7.2	Quantum Dynamics in Fluctuating Environments	260
7.2.1	System–Environment Models	261
7.2.1.1	Quantum Langevin equation	262
7.2.1.2	Spin-boson model	264
7.2.1.3	Bloch equations	266
7.2.2	Methods: RESPET and QUAPI	267
7.2.2.1	Weak coupling approximation	267
7.2.2.2	Correlated environmental fluctuations	269
7.3	Excitation Energy Transfer Dynamics	272
7.3.1	Energy Transfer in Donor–Acceptor Systems	274
7.3.1.1	Multiphonon transitions	275

7.3.1.2	Coherence due to temporal correlations	277
7.3.1.3	Influence of spatial correlations	278
7.3.2	Exciton Dynamics in the FMO Complex	280
7.3.2.1	Coherence times in the FMO complex	283
7.3.2.2	High-energy vibrations	285
7.4	Summary and Outlook	286
8	Excitation Energy Transfer in Light-Harvesting Systems: Theory, Models, and Application	293
	<i>Pengfei Huo and David F. Coker</i>	
8.1	Introduction	294
8.2	Partial Linearized Density Matrix Propagation	301
8.3	Model Hamiltonian	306
8.4	Short-Time Coherent Dynamics and Long-Time Thermal Equilibrium from PLDM Propagation	311
8.5	The Eight-Site FMO Complex: A Model for in vivo Initial Excitation	316
8.6	Strength of System–Environment Coupling Optimizes Energy Transfer Dynamic Turnover Behavior	319
8.7	Excitation Dynamics in Phycocyanin 645	321
8.8	Correlations between Site Energy Fluctuations	324
8.9	Concluding Remarks	329
9	Bridging the Gap between Coherent and Incoherent Resonance Energy Transfer Dynamics by Quantum Master Equations in the Polaron Picture	337
	<i>Seogjoo Jang</i>	
9.1	Introduction	337
9.2	System–Bath Hamiltonian and Formally Exact Quantum Master Equation	340
9.3	QME in the Weak System–Bath Coupling Limit	343
9.3.1	Time-Nonlocal Equation	343
9.3.2	Time-Local Equation	345
9.4	QME in the Polaron Picture	346
9.5	Practical Issues	354
9.5.1	Physical Observables in the Polaron Picture	354
9.5.2	Assessment of Quantum Coherence	356

9.5.3	Numerical Implementation	356
9.6	Model Calculations	357
9.6.1	Two-State System	357
9.6.2	Three-State System	361
9.7	Applications	364
9.8	Summary and Outlook	366
10	Theory of Metal Nanoparticle–Affected Optical and Transport Properties in Supramolecular Complexes	371
	<i>Yuan Zhang, Yaroslav Zelinsky, Gerold Kyas, and Volkhard May</i>	
10.1	Introduction	371
10.2	Collective Excitations of Metal Nanoparticle Electrons	376
10.2.1	Description of Dipole Plasmons	376
10.2.2	Description of Multipole Plasmons	378
10.3	Molecule Metal Nanoparticle Coupling	381
10.4	Description of a Spherical MNP	384
10.4.1	Coupling of an SC to a Spherical MNP	384
10.5	Photoinduced Processes in a Supramolecular Complex Coupled to a Metal Nanoparticle	385
10.5.1	Density Matrix Theory	388
10.5.2	Photoinduced Excitation Energy Transfer	389
10.5.3	Linear Absorption	393
10.5.4	Emission	395
10.6	Concluding Remarks	401
11	Ultrafast Energy and Charge Transfer in Functional Molecular Nanoscale Aggregates	407
	<i>Hiroyuki Tamura, Keith H. Hughes, Rocco Martinazzo, Jan Wahl, Robert Binder, and Irene Burghardt</i>	
11.1	Introduction	407
11.2	Electron–Hole Lattice Hamiltonian	410
11.2.1	Electron–Hole Basis	410
11.2.2	Wave Functions and Density Matrix Representation	412

11.2.3	Vibronic Hamiltonian in the e–h Basis	413
11.2.4	Effective-Mode Reduction Techniques	416
11.3	Quantum-Dynamical Calculations Using Multiconfigurational Methods	419
11.4	Exciton Migration and Relaxation at a Torsional Defect Site	420
11.4.1	Hamiltonian	421
11.4.2	Ultrafast Exciton Relaxation	422
11.5	Exciton Dissociation at an Oligothiophene–Fullerene Junction	424
11.5.1	Hamiltonian	425
11.5.2	Primary Exciton Break-Up Step	425
11.5.3	Formation of Charge-Separated States	426
11.6	Conclusions and Outlook	429
12	Ultrafast Spectroscopy: Quantum Information and Wave Packets	437
	<i>Joel Yuen-Zhou, Jacob J. Krich, Ivan Kassal, and Alán Aspuru-Guzik</i>	
12.1	Introduction	438
12.2	The Quantum Process Matrix χ	439
12.2.1	Properties and Examples	440
12.2.2	QPT Algorithms	442
12.3	The Model System	443
12.4	Frequency-Integrated Pump–Probe Spectroscopy	449
12.5	Relationship between Frequency-Integrated $P P'$ Spectra and the Process Matrix $\chi(T)$	456
12.6	Conclusions	462
13	Simulating the Nonlinear Optical Response of Multichromophore Complexes	467
	<i>Arend G. Dijkstra and Yoshitaka Tanimura</i>	
13.1	Two-Dimensional Spectra in the Limit of a Fast Environment	468
13.2	Classical and Adiabatic Environment: Vibrations in Peptides	472

13.3	Quantum Environment: Electronic Excitations in Molecular Aggregates	477
13.4	Nonlinear Spectra: Correlations and Line Shape	483
13.5	Conclusion	487
	<i>Index</i>	489

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 photoreceptor 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.

Irene Burghardt

Stefan Haacke

Frankfurt and Strasbourg, July 2016