PREFACE

The investigation of structures and properties of nucleic acids has fascinated and challenged researchers ever since the discovery of their relation to genes. Extensive studies have been carried out on these species to unravel the mystery behind the selection of these molecules as genetic material by nature and to explain various physico-chemical properties. However, a vast pool of information is yet to be discovered. DNA constituents, mainly aromatic purine and pyrimidine bases, absorb ultraviolet irradiation efficiently, but the absorbed energy is quickly released in the form of ultrafast nonradiative decays. Recently impressive progress has been made towards the understanding of photophysical and photochemical properties of DNA fragments.

It has been established that the singlet excited state life-times of nucleic acid bases are in the sub-picosecond range. These state-of-the-art experiments became feasible due to the advancement of electronics technologies, the advent of femtosecond lasers and the development of advanced methodologies to vaporize volatile compounds like the nucleic acid bases in order to trap them in supersonic jet expansion. Theoretical studies on DNA fragments have revealed valuable and subtle details, many of which are still not accessible by experiments. For example, ground state geometries of nucleic acid bases were determined experimentally using X-ray crystallography and neutron diffraction a long time ago, but quantitative information about excited state geometries of such complex molecules using experimental techniques is still not possible. Only limited information (e.g. nonplanarity) based on resonance Raman spectroscopy and the diffuseness of R2PI spectra with regard to the excited state geometries has been obtained. On the other hand, using theoretical methods, one can predict excited state geometries of complex molecules (within the limits of the available computational resources), which indicate that DNA bases are generally nonplanar in the singlet electronic excited states.

However, it should be noted that routine computation of excited state properties at the *ab initio* level has become feasible only recently due to the impressive development of computer hardware and computational algorithms. Applicability of theoretical methods to investigations of the ground state properties is relatively much simpler than to excited states. Usually single-reference methods are suitable

for studying ground state properties, although dynamical electron correlation has to be included for chemical accuracy. To study excited states of molecules, generally multiconfigurational methods are needed. This is particularly important in exploring conical intersections where potential energy surfaces have multiconfigurational nature. Further, to obtain spectral accuracy, dynamic correlation is also necessary. These requirements considerably hamper an extensive investigation of excited state phenomena.

This volume covers exciting theoretical and experimental developments in the area of radiation induced phenomena in nucleic acid fragments and selected related species. It mainly focuses on the effects of ultraviolet radiation and low-energy electrons on DNA fragments that include nucleic acid bases and nucleosides. These contributions have been delivered by experts in a wide range of subfields extending from *ab initio* theoretical developments, excited state molecular dynamics simulations, experiments unraveling ultra-fast excited state phenomena, nonradiative deactivation mechanisms and low energy electron induced DNA damage.

The first chapter, written by the editors of this book, is devoted to a brief introduction of UV and low energy electron induced phenomena in DNA fragments. It also provides a brief synopsis of all contributions in the volume which can serve as a guide for less experienced readers. The second chapter, contributed by S. Hirata et al., provides a lucid presentation of single-reference methods currently in use for excited state calculations and discusses their advantages, weaknesses and strategies for further improvements. This chapter is followed by contributions dealing with highly electron correlated methods such as different variants of the coupled-cluster method by J.D. Watts and the Symmetry-Adapted Cluster-Configuration Interaction (SAC-CI) method by J. Hasegawa and H. Nakatsuji. B.O. Roos has been instrumental in the development of CASSCF and CASPT2 multiconfiguration methods and he has contributed the next chapter. It is followed by a chapter written by M. Abe et al. dealing with the development of relativistic multireference perturbation theory. R. Cammi and B. Mennucci, who are among leading researchers involved in the development and implementation of different solvation models, discuss the PCM solvation model and its application to electronic excited states of molecular system in Chapter 7.

The next three chapters deal with the developments and applications of excited state molecular dynamics techniques for studying nucleic acid fragments and model systems. M. Barbatti et al. have discussed nonadiabatic excited state dynamics investigation of aromatic heterocycles. B.E. Billinghurst, S.A. Oladepo and G.R. Loppnow have discussed the application of Raman and resonance Raman spectroscopic methods for predicting the excited state structural dynamics of nucleic acid components. On the other hand, N.L. Doltsinis et al. have discussed the results of *ab initio* molecular dynamics simulations unraveling the nonradiative decay of nucleic acid fragments. We also have three contributions from experimentalists who have performed seminal work using advanced technologies and spectroscopic methods to study excited state structures and properties of nucleic acid bases, base

pairs and related species. These contributions also discuss the principles of different experimental methodologies used in the investigations. W. Kong, Y. He and C. Wu have discussed different deactivation pathways of pyrimidine bases both in the gas phase and in solution. M.S. de Vries has discussed results of advanced spectroscopic investigations and applications of theoretical methods in exploring the structural information from the complex spectra of nucleic acid bases and base pairs. Guanine is the nucleic acid base that has the largest number of tautomers detected in different environments. Interestingly, the recent reassignment of the R2PI spectra shows the existence of relatively less stable imino tautomers in the jet-cooled supersonic beam. The contribution from M. Mons, I. Dimicoli and F. Piuzzi provides a comprehensive description of experimental and theoretical analysis of guanine tautomerism in the gas phase. This chapter is followed by a brief analysis of electronic transitions, excited state geometries, hydration and proton transfer in DNA bases and electronic excited state structures of thio analogs of bases presented by the editors.

Recently, there have been impressive activities focusing on understanding the ultrafast nonradiative processes in nucleic acid bases and base pairs using high level theoretical methods. This volume presents three contributions dealing with up-to-date information on different possible mechanisms for the ultrafast deactivations of DNA fragments. A comprehensive analysis of experimental and theoretical results explaining the nonradiative deactivations and the prominent role played by biradical states of DNA bases, donor-acceptor species and other biological systems is the focus of the contribution from M.Z. Zgierski, T. Fuziwara and E.C. Lim. On the other hand, an application of highly correlated methods unraveling nonradiative decay mechanisms of DNA bases and base pairs, singlet-triplet crossing and photodimerization is discussed by L. Serrano-Andrés and M. Merchán. L. Blancafort, M.J. Bearpark and M.A. Robb discuss the results of highly electron correlated methods in the exploration of different possible nonradiative deactivation routes in cytosine.

The last part of the book discusses low energy electron induced DNA damage and the possible mechanisms of such phenomena. D.M. Close discusses experimental methods and theoretical analysis of radical formation of the DNA fragments. L. Sanche, who discovered that low energy electrons can also produce DNA strand breaks, presents a comprehensive analysis of different experiments dealing with low energy electron induced DNA damage. Theoretical analysis of different possible mechanisms for low energy electron induced DNA damage is presented by A. Kumar and M.D. Sevilla. The last chapter, contributed by J. Rak et al., presents a lucid analysis of experimental and theoretical results obtained from the study of electron induced DNA damage including different possible pathways.

With a great pleasure, we take this opportunity to thank the contributing authors for devoting their time and hard work to enable us to complete this volume. We believe that with excellent contributions from all the authors, this book provides a common platform for both theoreticians and experimentalists. We hope that it

will be useful not only for those involved in this area, but also for others who are planning to launch research on excited state properties of complex molecules. As usual, graduate students are also our important target audience. We are grateful to the editors at Springer for excellent cooperation and to our families and friends for their kind support.

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