



PAPER

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Dispersion-induced structural preference in the ultrafast dynamics of diphenyl ether†

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Dispersion interactions are omnipresent in large aromatic systems and influence the dynamics as intermolecular forces. The structural preference induced by dispersion interactions is demonstrated to influence the excited state dynamics of diphenyl ether (DPE) using femtosecond time-resolved transient absorption (TA) associated with quantum chemical calculations. The experimental results in aprotic solvents show that the S_1 state is populated upon irradiation at 267 nm with excess vibrational energy dissipating to solvent molecules in several picoseconds, and then decays via internal conversion (IC) within 50 ps as well as intersystem crossing (ISC) and fluorescence with a lifetime of nanoseconds. The polarity of the solvent disturbs the excited state energies and enhances the energy barriers of the ISC channel. Furthermore, the intermolecular dispersion interactions with protic solvents result in the OH- π isomer dominating in methanol and the OH-O isomer is slightly preferred in *t*-butanol in the ground state. The hydrogen bonded isomer measurements show an additional change from OH-O to OH- π geometry in the first 1 ps besides the relaxation processes in aprotic solvents. The time constants measured in the TA spectra suggest that the OH-O isomer facilitates IC. The results show that the OH- π isomer has a more rigid structure and a higher barrier for IC, making it harder to reach the geometric conical intersection through conformer rearrangement. This work enables us to have a good knowledge of how the structural preference induced by dispersion interactions affects excited state dynamics of the heteroaromatic compounds.

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Introduction

Non-covalent interactions have been recognized as a very important factor in molecular recognition and aggregation processes,^{1–4} as well as the three-dimensional structure of proteins and DNA, which determines the function of these biomacromolecules.^{5,6} Undoubtedly, they determine deactivation pathways in light-driven processes. The chromophore of the green fluorescent protein can only emit fluorescence in the environments of noncovalent interactions with surrounding proteins, but not in the free condition without interactions.^{7–10} Hydrogen bonding and dispersion interactions, as important non-covalent interactions, act on the molecular systems individually or jointly and have attracted much attention.^{11–13} Hydrogen bonds have been proved to be of great significance in IC, photoinduced electron transfer, charge transfer, fluorescence quenching, etc.^{14–16} The formation of the hydrogen-bonded complex may be essential for the photoinduced

reaction. It is reported that the intermolecular hydrogen-bonded aggregates of catechol elongate the lifetime for dissociation because of the excited state structural relaxation.^{17,18} However, dispersion interactions are ubiquitous in the chromophore-environment interactions but often neglected as inter- or intramolecular forces. In fact, dispersion forces sum up as the molecular size becoming larger and are comparable to the hydrogen bond in the large aromatic systems.¹⁹ The impact of the intramolecular dispersion interactions on the photochemical processes has been verified with theoretical calculations.²⁰ Intramolecular dispersion interactions can shape the potential energy surface and the structural evolution of the photoexcited stilbene and its substituted derivatives, thus increasing the ratio of the photocyclization pathway. The effect of the solute-solvent dispersion interactions on the solute dynamics remains unclear. Two-type intermolecular hydrogen bonding OH-O and OH- π isomers are formed in the heteroaromatic compounds.²¹ And the effect of the structural preference for the OH-O and OH- π interactions on the dynamics of the heteroaromatic molecules requires further exploring.

Because of the complexity of the intermolecular interactions in the large aromatic systems, the studies of dispersion interactions in small molecules have been concentrated using bottom-up approaches. Diphenyl ether (DPE) is a prototypical molecule for investigating the structural preference of hydrogen

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Structural Memory And The Dynamics Of Preference

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Structural Memory and the Dynamics of Preference Cornelis Cyrinus Van Leeuwen, 1989 **Handbook of Episodic Memory** Ekrem Dere, Alexander Easton, Lynn Nadel, Joseph P Huston, 2008-09-04 Episodic memory is the name of the kind of memory that records personal experiences instead of the mere remembering of impersonal facts and rules This type of memory is extremely sensitive to ageing and disease so an understanding of the mechanisms of episodic memory might lead to the development of therapies suited to improve memory in some patient populations Episodic memory is unique in that it includes an aspect of self awareness and helps us to remember who we are in terms of what we did and what we have been passed through and what we should do in the future This book brings together a renowned team of contributors from the fields of cognitive psychology neuropsychology and behavioural and molecular neuroscience It provides a detailed and comprehensive overview of recent developments in understanding human episodic memory and animal episodic like memory in terms of concepts methods mechanisms neurobiology and pathology The work presented within this book will have a profound effect on the direction that future research in this topic will take The first and most current comprehensive handbook on what we know about episodic memory the memory of events time place and emotion and a key feature of awareness and consciousness Articles summarize our understanding of the mechanisms of episodic memory as well as surveying the neurobiology of episodic memory in patients animal studies and functional imaging work Includes 34 heavily illustrated chapters in two sections by the leading scientists in the field The Structure, Dynamics and Function of Neural Micro-Circuits for Perception and Behavior Yoshiyuki Kubota, Allan T. Gullledge, M. Victoria Puig, 2022-10-05 *Social, Cultural, and Behavioral Modeling* Robert Thomson, Samer Al-khateeb, Annetta Burger, Patrick Park, Aryn A. Pyke, 2023-09-15 This book constitutes the proceedings of the 16th International Conference on Social Cultural and Behavioral Modeling SBP BRiMS 2023 which was held in Pittsburgh PA USA in September 2023 The 31 full papers presented in this volume were carefully reviewed and selected from 73 submissions The papers were organized in topical sections as follows Detecting malign influence human behavior modeling and social cyber behavior modeling *Preferences and Decisions* Salvatore Greco, Ricardo Alberto Marques Pereira, Massimo Squillante, Ronald R. Yager, 2010-10-05 Decision making is an omnipresent most crucial activity of the human being and also of virtually all artificial broadly perceived intelligent systems that try to mimic human behavior reasoning and choice processes It is quite obvious that such a relevance of decision making had triggered vast research effort on its very essence and attempts to develop tools and techniques which would make it possible to somehow mimic human decision making related acts even to automate decision making processes that had been so far reserved for the human beings The roots of those attempts at a scientific analysis can be traced to the ancient times but clearly they have gained momentum in the recent 50 or 100 years following a general boom in science Depending on the field of science decision making can be viewed in different ways The most general view can be that decision making boils down to

some cognitive mental processes that lead to the selection of an option or a course of action among several alternatives Then looking in a deeper way from a psychological perspective this process proceeds in the context of a set of needs preferences rational choice of an individual a group of individuals or even an organization From a cognitive perspective the decision making process proceeds in the context of various interactions with the environment *International Trade and Economic Dynamics* Takashi Kamihigashi, Laixun Zhao, 2008-10-16 Renowned trade theorist Koji Shimomura passed away in February 2007 at the age of 54 He published nearly 100 articles in international academic journals The loss of this extremely productive economist has been an enormous shock to the economic profession This volume has emerged from the great desire on the part of the profession to honor his contributions to economic research Contributors include authoritative figures in trade theory such as Murray Kemp Ronald Jones Henry Wan and Wilfred Ethier world renowned macroeconomists such as Stephen Turnovski and Costas Azariadis and leading Japanese economists such as Kazuo Nishimura Makoto Yano Ryuzo Sato and Koichi Hamada This broad range of contributors reflects Koji Shimomura's many connections as well as the respect he earned in the economic profession This volume offers the reader a rare opportunity to learn the views of so many renowned economists from different schools of thought **A Theory of the Inductive Learning of Multiattribute**

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Information Processing and Biological Systems Samuli Niiranen, Andre Ribeiro, 2011-03-10 Living beings require constant information processing for survival In cells information is being processed and propagated at various levels from the gene regulatory network to chemical pathways to the interaction with the environment How this is achieved and how information is coded is still poorly understood For example what a cell interprets as information in the temporal level of an mRNA and what is interpreted as noise remains an open question Recently information theoretical methods and other tools developed in the context of engineering and natural sciences have been applied to study diverse biological processes This book covers the latest findings on how information is processed in various biological processes ranging from information processing and propagation in gene regulatory networks to information processing in natural language An overview is presented of the state of the art in information processing in biological systems and the opinion of current leaders in this research field on future research directions

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