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INTERPLAY OF COMPUTATIONAL CHEMISTRY AND TRANSIENT ABSORPTION SPECTROSCOPY IN THE ULTRAFAST STUDIES

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The primary physical and chemical processes in the photochemistry of 1-(trideuteromethyl)-2,3,4-trideutero (**1**) and 1-acetoxy-2-methoxy- (**2**) 9,10-anthraquinones were studied using femtosecond transient absorption spectroscopy and computational chemistry. Excitation of **1** and **2** at 270 nm results in the population of a set of highly excited singlet states which decay within the laser pulse by internal conversion and vibrational energy redistribution. The transient absorption spectra of the lowest singlet and triplet excited states of substituted anthraquinones **1** and **2** as well as the triplet excited and ground states of the products were detected. The assignments of the transient absorption spectra were performed on the basis of quantum chemical calculations of the electronic absorption spectra of the intermediates. Time-dependent density functional theory or CASSCF/CASPT2 procedure were used to calculate the spectroscopic properties of the intermediates.

Keywords: femtosecond transient absorption spectroscopy, photochemical hydrogen transfer, photochemical acyl migration, electronic absorption spectra calculations, time-dependent density functional theory, CASSCF/CASPT2 procedure.

INTRODUCTION

There has been recent, dramatic progress in the development and application of computational methods in chemistry. To a great extent this is a result of the astonishing and unprecedented development of digital computer technology. Computational chemists have taken advantage of this progress to develop a number of new theoretical approaches and techniques and to build up a broad array of new theoretical tools. The synergy between theory and experiment leads to the acceleration and improvement of a number of areas of chemistry. For example, the field of the matrix isolation spectroscopy is now always accompanied with theoretical calculations of IR and UV-Vis spectra of proposed reactive intermediates [1, 2]. Quantum chemistry has been also extensively used for understanding and interpretation of the properties of reactive intermediates [3], including whose generated upon laser flash photolysis [4].

However, computational methods have been infrequently applied to the interpretation of the results of ultrafast studies in the femto- and picosecond time domains. This is caused, in part, by the fact that excited state intermediates are usually the only species detected on this time scale. Open-shell species are the most challenging molecules for quantum

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