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Revisiting magnetic field effects in homogeneous medium and bio-mimicking environments with emphasis on acridine derivatives[☆]



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ABSTRACT

A weak external magnetic field, very close to the hyperfine interactions of the system, can act as a tool to monitor spin dynamics and assess distance between the components of the spin-correlated transient radical pair or radical ion pair (RIP). The present review focuses on the magnetic field effect (MFE) on the photo-induced electron-transfer (PET) reactions among acridine derivatives and classical as well as biological electron acceptor or donor moieties, which produce spin-correlated RIPs, in homogeneous solvents, heterogeneous micellar media and in biological nanocavities of proteins. Although a confined medium is preferred to observe prominent MFE, yet unanticipated MFE on PET between acridine derivatives [Acridone (AD) and Acridine Yellow (AY)] and classical electron donors is obtained even in homogeneous medium when it consists of impurities like water molecules. In a comparative study of interaction of another acridine derivative, Proflavin (PF⁺) with two electron donors which are amines of aromatic nature, MFE on PET reveal that the bulk and the structure of the electron donor govern the mechanism as well as the spin dynamics of PET. While studying interaction of PF⁺ with a different amine which is aliphatic in nature, MFE on PET implies that it is the nature of the solvent matrix which determines the spin dynamics of PET. The cause of discrepancy in the experimental and calculated values of $B_{1/2}$ for 9-amino acridine – methyl viologen system has been delineated. Apart from micellar medium, prominent MFE on PET is also observed while studying the interaction of PF⁺, AY and AD with tryptophan residues present in the nanocavities of serum albumins since the inter-radical distance within primary geminate RIP is enough to make exchange interaction negligible.

1. Introduction

As the phenomenon of Photo-induced Electron-Transfer (PET) reactions is extensively prevalent in chemical and biological sciences, understanding as well as control of these reactions is a thriving area of research today. PET involves electron transfer from an electron rich donor to an electron deficit acceptor, while one of them remains in the photo-excited state. It may be either intermolecular, i.e. occurs between two separate molecules serving as electron donor and acceptor or intramolecular when both the donor and the acceptor are parts of the same molecule linked with a spacer. In general, PET is identified by quenching of fluorescence. However, as a consequence of PET, non-fluorescent radical pairs (RPs) or radical ions pairs (RIPs) (or in some cases combination of radical and radical ion) are formed as intermediates in the reaction pathway. These non-fluorescent transients (short-lived) species

can be detected not by steady-state fluorescence, but by using transient absorption techniques, among which nanosecond-resolved laser flash photolysis (LFP) is quite popular and easy to handle. Thus, the occurrence of PET may be confirmed via detection of the presence of radical/radical ions in the system. As radicals/radical ions contain free electrons, so they are prone to be perturbed by an externally applied magnetic field (MF) [1–4]. A weak MF in the range of 0.01–0.08 T has an enormous capacity to modulate the reaction pathways containing radicals/radical ions by manipulating their spin dynamics. The magnetic field effect (MFE) is a subtle amalgamation of dynamics of diffusion and spin of the initially formed geminate radical pairs originating from PET. The geminate radical pairs or radical ions pairs within solvent cage are individually disintegrated through diffusion in the solvent and achieve an ideal distance where the interaction through exchange (J) becomes negligible and the MF present within the system generated through electron and nuclear

[☆] This review article is dedicated to Professor Dulal Chandra Mukherjee.

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