

# Magnetic Field Effects in Fluorescence of Exciplex and Fluorophore for the Weller Schemes I and II: Similarities and Differences

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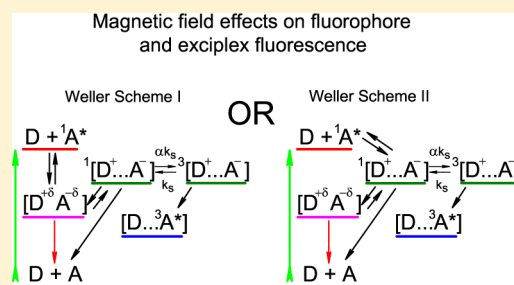
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**ABSTRACT:** In exciplex-forming donor–acceptor systems the photoexcited acceptor state can be quenched either by exciplex formation at the contact of the acceptor and the donor, followed by reversible dissociation to the radical-ion pair (Scheme I), or by distant electron transfer yielding a radical-ion pair that can reversibly recombine to produce an exciplex (Scheme II). The fluorescence of the photoexcited electron acceptor (fluorophore) and the exciplex is known to be sensitive to the magnetic field, assisting spin conversion in the resulting geminate radical-ion pair (RIP). An increase of the fluorescence yield in high magnetic fields compared to low fields is known as the magnetic field effect (MFE). In this paper theories of the MFE on both the fluorophore and the exciplex within the Schemes I and II are developed. Kinetics of the reversible reactions are described in terms of the integral encounter theory that unlike the differential encounter theory is capable of dealing with such reactions. Regions of the parameters where MFE is observable are discussed. Comparison of functional dependencies of MFE on the model parameters for the Schemes I and II is carried out. Magnitudes and dependencies of MFE on the model parameters are found to be very similar for the Schemes I and II, except the dependencies of the fluorophore and exciplex MFEs on the rate constant of exciplex production from the radical-ion pair, which appear to be opposite for the Schemes I and II.



## I. INTRODUCTION

Electron transfer (ET), being the simplest and a widespread reaction in artificial and biological systems, has been extensively investigated for several decades.<sup>1–5</sup> These investigations not only have provided an understanding of bimolecular photoinduced reactions but also have uncovered a series of promising applications, among them organic solid-state photovoltaic and other molecular optoelectronic devices.<sup>6–10</sup> Great efforts to study these processes have resulted in a deep understanding of the physical processes accompanying the charge transfer in solutions. Nevertheless, some important questions are still to be answered. Among them is the question in which sequence radical-ion pairs (RIPs) and exciplexes are formed in photoinduced electron transfer.<sup>11–16</sup> Exciplexes composed of a strongly coupled pair of the partially charged donor,  $D^{+\delta}$ , and the acceptor of the electron,  $A^{-\delta}$ , are produced in many photochemical reactions and manifest themselves through their specific fluorescence that allows monitoring their population kinetics. Besides, the exciplex fluorescence is sensitive to the external magnetic field, which is known as the magnetic field effect (MFE).

MFE in chemical reactions with radical-forming stages has received considerable attention in the last decades.<sup>19–28</sup> It is a common point of view now that the magnetic-sensitive stages of these reactions involve singlet–triplet transformations in RIPs. From the singlet precursor, the geminate RIP is initially produced in its singlet state due to conservation of the overall spin,<sup>19</sup> but when the distance between the RIP partners in solution becomes sufficiently large and their exchange coupling weakens, the hyperfine interaction can induce coherent singlet–triplet transitions in it. The external magnetic field, lifting the  $S-T_{\pm}$  degeneracy to a sufficient extent, can significantly suppress singlet-to-triplet transformations in RIPs because only one  $S-T_0$  conversion channel of three remains operative. This results in a slower rate of singlet–triplet conversion in strong magnetic fields (for organic systems, on the order of tens of millitesla). Because the part of the RIPs remaining in the singlet state in this case is larger, their

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