

Preface

Radiation chemistry is concerned with understanding the chemical kinetics following the application of ionising radiation. There are two main methods for modeling recombination and spin dynamics in radiation chemical systems: The Monte Carlo random flights algorithm, in which the trajectories of the diffusing species are followed explicitly and the Independent Reaction Times (IRT) algorithm, where reaction times are sampled from appropriate marginal distribution functions. This thesis reports developments to both methods, and applies them to better understand experimental findings, particularly spin relaxation effects.

Chapter 4 introduces current simulation techniques and presents newly developed algorithms and simulation programs (namely *Hybrid* and *Slice*) for modeling spatially dependent spin effects. A new analytical approximation for accurately treating ion-pair recombination in low-permittivity solvents is also presented in this chapter.

Chapter 5 explores the photodissociation of H_2O_2 , where there is some controversy in the literature on the spin state of the precursor. This chapter explores the possibility of reproducing the observed spin polarization phase using the Radical Pair Mechanism.

Chapter 6 presents two new algorithms for treating reactive products in the IRT framework. These have been tested for two chemical systems: (i) photodissociation of H_2O_2 where the $\cdot\text{OH}$ are scavengeable; (ii) water photolysis which produces H^+ , $\cdot\text{OH}$ and e_{aq}^- . In the latter case a careful handling of three body correlations is required.

Chapter 7 presents simulation results, which suggest a strong correlation between scavenging and ion recombination in low permittivity solvents (a fundamental breakdown of the assumptions underlying the theory of diffusion kinetics). A path decomposition method has been devised that allows IRT simulations to be corrected for this effect.

Chapter 8 presents evidence for spin-entanglement and cross-recombination to act as an extra source of spin relaxation for ion-recombination in low permittivity solvents. It is hypothesized that this effect contributes to the anomalous relaxation times observed for certain cyclic hydrocarbons.

[Chapter 9](#) presents an extension of the IRT simulation method to micelles. The kinetics are shown to be accurately described using the mean reaction time and the exponential approximation.

Simulation Studies of Recombination Kinetics and Spin
Dynamics in Radiation Chemistry

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