MAGNETIC FIELD EFFECTS ON FLUORESCENCE: APPLICATION OF MARY-SPECTROSCOPY TO ELECTRON TRANSFER KINETICS

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Electron self-exchange between a molecule and its corresponding radical cation or anion:

\[ \text{A} + \text{A}^+ \rightarrow \text{A}^+ + \text{A} \]

when it is part of a spin-correlated radical pair gives rise to linewidth effects in the MARY (MAgnetic field effect on Reaction Yield) spectrum, similar to those observed in EPR. The lifetime of a given nuclear spin configuration that couples to the electron spin decreases with increasing self-exchange rate (i.e. concentration of molecule), leading to broadening and subsequent narrowing of the spectrum. Applying a method outlined in [1], self-exchange rate constants have been determined from the initial slope of the plot of linewidth vs. concentration for a variety of radical pair systems, including pyrene/dicyanobenzene (DCNB) isomers [2] and N-alkylcarbazole/DCNB [3]. The observed rate constants show a dependence on the solvent as well as on the radical pair partner that does not take part in the exchange, whereas the magnitude of linebroadening is related to the average hyperfine coupling constant of the exchanging radical.

Experimental results are compared with theoretical simulations using two different approaches: first, a quantum mechanical method based on a density matrix formalism [4] is applied to a two-proton radical pair. Second, the extension of a semiclassical model [5] allows the calculation of the MARY spectra of the systems that have been investigated experimentally. Both models reproduce the observed linewidth effects.

References