Unified Theory of Bridge Mediated Electron Transfer

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A unified theoretical description is presented for electron transfer (ET) reactions mediated by molecular bridges. The approach is based on a general nonequilibrium statistical theory and ends with kinetic equations and respective ET rate expressions. The latter account for the superexchange mechanism of ET as well as for the sequential (hopping) ET or, alternatively, for thermally activated ET (in the particular case of large electronic couplings among the bridge units) /1, 2, 3/.

It is first demonstrated that for integral bridge populations less than 10^{-3} the whole ET process can be reduced to single-exponential kinetics described by an effective D-A transfer rate. This rate contains contributions from the sequential (or thermally activated) as well as the superexchange mechanism, and thus can be used for a quantitative analysis of the efficiency of different electron pathways. For room-temperature conditions and if the number of bridge units exceeds 4 or 5 the superexchange mechanism is replaced by the sequential (or thermally activated) one. The theory is applied to experiments on ET through a peptide bridge of proline oligomers with varying length /2, 4/. The influence of structural and energetic disorder is also described /5/.

In a second part the given approach is extended to a study of two-electron transfer (TET) reactions. As an example of such TET processes the reduction of micothione reductase by NADPH is analyzed resulting in a nice description of existing experimental data /6/. Furthermore, it is demonstrated how the concepts of bridge-mediated ET may be used to achieve a better understanding of charge motion through nano-electrode contacted molecular wires /7, 8/.

Ultrafast bridge mediated ET and its possible control by femtosecond laser pulses is finally mentioned /9/.

References

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