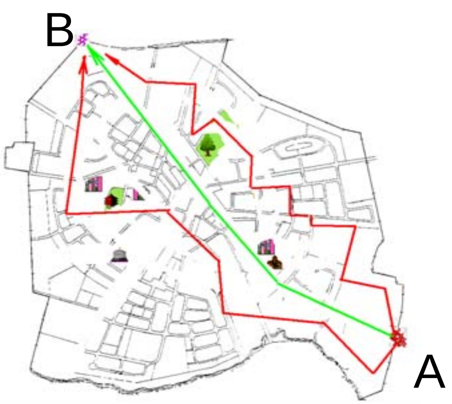
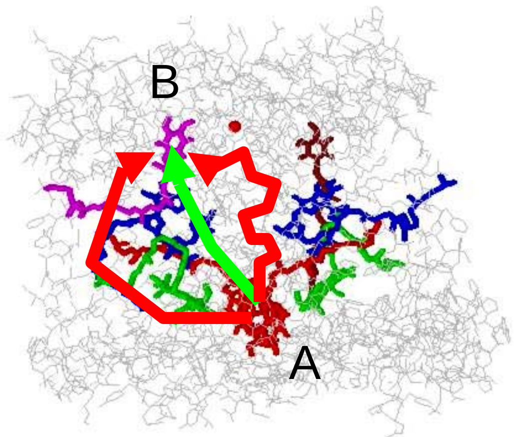
Mapping Electron Transfer Pathways in Photosynthesis

In photosynthesis, the primary energy conversion reactions involve a photoinitiated sequence of efficient electron-transfer steps resulting in charge separation across a biological membrane, thus converting light into an electrochemical potential. These biological electron transfer reactions occur between cofactors (electron-holding molecules) that are encased within a well-ordered protein "scaffolds". The protein amino acid environments surrounding the cofactors have been tuned by biology to provide optimal pathways for electron transfer and solar energy conversion. Up to now chemists have been limited in their ability to see the pathways for electron transfer between cofactors in photosynthetic proteins and to resolve how protein environments contribute to highly efficient solar energy conversion.

Using specialized magnetic resonance spectroscopies, we have discovered a new method for directly detecting magnetic interactions between electron-holding cofactors and amino acid environments, thus allowing electron transfer pathways to be mapped within photosynthetic proteins. This new method will enable us to explore the fundamental mechanisms for highly efficient light-induced electron transfer and energy conversion in photosynthesis, and it will facilitate the design of biomimetic artificial photosynthesis.





As with a road-map where there are multiple paths for travel between points A and B, including those that are more (green) or less (red) efficient, there are multiple pathways possible for electron transfer between cofactors (red, blue, purple molecules) in proteins (gray lines). Argonne's magnetic resonance technique provides a new way to directly detect electron transfer paths in proteins.

Poluektov O. G., Utschig L.M. Dubinskij A.A., Thurnauer M.C.
"ENDOR of Spin-Correlated Radical Pairs in Photosynthesis at High Magnetic Field: A Tool for Mapping Electron Transfer Pathways"
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