Radical quantum oscillations

Laser spectroscopy reveals spin quantum beats in electron transfer reactions

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Chemical reactions can be accelerated by weakening chemical bonds in the reactant molecules, which can be done by increasing their thermodynamic free energy. However, nothing much will happen if the increase in free energy per molecule is much less than the thermal energy (Boltzmann's constant times temperature). Therefore, it may be surprising that magnetic interactions 100,000 times smaller than the thermal energy can influence the course of certain chemical transformations (*1*, *2*). The reason that some reactions can be so sensitive to weak magnetic fields lies in the oscillations between different electronic states of the reaction intermediates. These oscillations, known as "quantum beats," occur at frequencies around 10 MHz and play a pivotal role in these exceptions to the rule (*3*, *4*). On page 1470 of this issue, Mims et al. (*5*) report a technique for revealing these normally hidden oscillations and providing insights into this intriguing class of reactions.

Radicals – molecules that contain an odd number of electrons – can be formed as pairs, for example, when one molecule transfers an electron to another molecule. In particular, organic radical pairs have distinctive features that give rise to their unusual behavior. The pair can exist as singlet or triplet states, i.e. possessing antiparallel or parallel electron spins, whose reactions obey selection rules in which spin is conserved. Moreover, if the radicals are not too close together, the singlet and triplet states, because of their similar energies, would interconvert coherently in a process known as quantum beating, which can be fine-tuned by weak magnetic interactions. The singlet and triplet fractions beat at frequencies characteristic of the magnetic fields experienced by the electrons. One source of these fields is the hyperfine interactions with the spins of atomic nuclei such as hydrogen and nitrogen. Another is the Zeeman interaction with externally applied magnetic fields.

Because the thermodynamic constraint mentioned above does not apply to radical pairs when the spins are far from equilibrium with their surroundings, weak magnetic interactions therefore control the instantaneous probability of the radical pair being singlet or triplet, as well as the likelihood for the pair to react spin-selectively to form distinct singlet or triplet products. The yields of the two competing reaction pathways depend in a complex fashion on the timing of the coherent spin dynamics. A frustrating aspect of the radical pair mechanism is that it is rarely possible to observe these quantum beats directly. To do so, one would need to differentiate between the two states using, for example, ultrafast electronic spectroscopy (*6*, *7*). However, this is normally impossible because singlet and triplet pairs have very similar energies, often within 10^{-6} eV, such that their absorption spectra are indistinguishable. It is easier to tell the reaction products apart but as they are usually formed on a timescale much slower than singlet-triplet interconversion, any oscillations in their concentrations are seldom apparent.

The "pump-push" technique devised by Mims et al. avoids these obstacles by using laser pulses to provide snap-shots of the spin state of the radical pair at different times after its creation. Radical pairs are produced, initially in a singlet state, by a short flash of light, known as the "pump," which causes an electron to jump from a donor molecule to an acceptor. Coherent spin motion ensues, driven by hyperfine interactions. After a variable delay, the radicals are subjected to a second short, strong laser flash with a longer wavelength, i.e. the "push" pulse. The result, for both singlet and triplet states, is an electronically excited and much more reactive radical pair, which undergoes rapid and spin-selective reverse electron transfer. If the "pushing" and the ensuing reactions are both faster than the spin motion, this effectively instantaneous sampling of the spin state of the radical pair would be detectable as an abrupt change in the absorption or fluorescence of the donor and/or acceptor. By repeating the measurement with different pump-push delays, one can map out the coherent spin dynamics.

The molecule selected for these proof-of-principle experiments comprised an aromatic tertiary amine electron donor and a perylene diimide electron acceptor separated by a dihydroanthracene bridge. Although structurally complex, the radical pair has a beautifully simple spin system. The hyperfine fields that drive the coherent spin dynamics are dominated by a single nitrogen in the donor radical, with a smaller contribution from four identical hydrogens in the acceptor radical. This simplicity ensures a small number of quantum beat frequencies which are more easily recorded than in the case of radicals with many coupled nuclei.

The pump-push method has many potential applications. It could be used to investigate photoactive proteins known as cryptochromes that, among other things, regulate plant growth and circadian rhythms. Many cryptochromes bind a flavin adenine dinucleotide cofactor, excitation of which with blue light triggers three or four sequential electron transfers along a chain of tryptophan amino acid sidechains within the protein. The radical pair so formed shows pronounced magnetic sensitivity down to the millitesla range (*8, 9*) and has been proposed (*10, 11*) as the receptor that allows migratory songbirds to sense the direction of the Earth's magnetic field (*12*). Direct observations of the coherent spin motion would reveal otherwise obscured information on the origin of the magnetic sensitivity. The pump-push method is also likely to find rewarding applications in studying magnetic field effects on electron-hole pairs in organic light-emitting diodes whose magnetoresistance and magneto-electroluminescence can be explained by the radical pair mechanism (*13*).

Another potential application, relevant in the emerging field of quantum biology (*14*), might be to determine the extent to which radical pair magnetoreception is truly quantum. This question was recently approached by asking whether one can only account for the coherent spin dynamics in cryptochromes using quantum mechanics or whether a description using classical oscillations would suffice (*15*). A more satisfactory answer could be provided by measuring the quantum beats instead of inferring them from the yields of reaction products.

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Observing quantum beats in the reactions of radical pairs

Coherent interconversion of the singlet (↑↓) and triplet (↑↑) states of radical pairs normally hidden from view. Mims *et al*. reveal these oscillations by using “pump” and “push” laser pulses to move an electron from one end of a donor-bridge-acceptor molecule to the other and back again.