

photochemical reactions. Reactions such as atom and proton transfer, electron transfer and energy transfer are likely candidates as long as their photochemical process occurs on a timescale of a few picoseconds or less. This coherent picture is unique in that after vertical Franck–Condon excitation by the photon, the temporally phased motion of the molecule along critical reactive vibrational degrees of freedom, like the torsion and HOOP modes in rhodopsin, directs the molecule to the conical intersection with precisely the correct trajectory in phase space to effect efficient and rapid passage through it — as depicted in Fig. 1.

While the concept of a ‘phase-space trajectory’ may seem foreign, we have all experienced it personally. When an

airplane turns to land on a runway, the pilot is executing a precise (we hope) trajectory in a six dimensional ‘phase space’ made up of the plane’s x , y , and z coordinates and the associated velocities. Touching down at the correct spot on the runway is analogous to hitting the conical intersection with just the correct vibrational coordinates and momenta to effect surface crossing.

Returning to the vibrationally coherent molecular flight of retinal in rhodopsin, the initial phase-space trajectory is determined by the slopes of the potential energy surface in the Franck–Condon excitation region⁷. Local couplings and anharmonicities in the vicinity of the conical intersection serve to redirect and redistribute this initial trajectory thereby also playing a role in

determining the yield and timescale of photoproduct appearance. Rhodopsin is indeed a paradigmatic photochemical molecule that continues to teach us new lessons about reaction mechanisms. □

*Richard A. Mathies is in the Department of Chemistry, University of California at Berkeley, Berkeley, California 94720, USA.
e-mail: ramathies@berkeley.edu*

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2015 NOBEL PRIZE IN CHEMISTRY

Requiring repair



HHMI/KEVIN WOLF



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DNA strands are used by all living organisms to store genetic information that is crucial for cellular function, development and reproduction. These strands can contain millions of base pairs that provide a vast array of sites at which errors can be introduced or damage can occur. Preventing such blemishes from persisting and accumulating is therefore essential for life — but the mechanisms by which organisms reverse damage to DNA was not always clear. Now, Paul Modrich, Tomas Lindahl and Aziz Sancar (pictured left–right) have been jointly awarded the 2015 Nobel Prize in Chemistry for their pioneering ‘mechanistic studies of DNA repair’.

Although it was known that DNA could be degraded, scientists in the 1970s

thought that it was a very stable molecule. Tomas Lindahl of the Francis Crick Institute and Clare Hall Laboratory, Hertfordshire, UK, showed that in fact DNA has limited chemical stability and that it deteriorates at a rate that should make life impossible. He therefore reasoned that there must be mechanisms by which damage to DNA is reversed. Later, he uncovered how a process called base excision repair works. In this process damaged DNA bases are recognized and removed by enzymes prior to the DNA strand being repaired.

Aziz Sancar, University of North Carolina, USA, discovered another mechanism by which DNA is repaired called nucleotide excision repair. In this mechanism a short section of single-stranded DNA is removed

and then replaced using the opposite strand as a template. Nucleotide excision repair is an important repair mechanism because it can remove DNA adducts caused by mutagenic chemicals or UV light.

The contribution of Paul Modrich, of the Howard Hughes Medical Institute and Duke University School of Medicine, USA, was to uncover another mechanism called mismatch repair. The mismatch repair machinery improves the fidelity of DNA replication by around 1000-fold as it enables DNA bases that have been incorrectly incorporated during DNA replication to be replaced.

RUSSELL JOHNSON