Molecular Orbitals Tell the Story

James N. O’Shea

To understand the rich physics of molecular nanostructures and solids, there are times when high-resolution photoemission data are all we need to build a detailed picture of the electronic structure. At other times, structural information from x-ray diffraction or scanning tunneling microscopy (STM) can reveal precisely what is going on at the molecular level. But the most intriguing questions often leave us wishing that we could simply get in there and take a good look at the single-molecule level. On page 468 of this issue, Wachowiak et al. describe how they have done precisely this in order to observe the molecular distortion in an insulating monolayer of $K_3C_{60}$ by using a combination of topographic and spectroscopic STM at low temperature (1).

The particular distortion in question results from the Jahn-Teller (JT) effect, a phenomenon with a long history. JT distortions arise when a system is degenerate—that is, it exhibits two or more distinct states with exactly the same energy. Nature tries to avoid this situation if there is an energy saving to be made by a molecule undergoing a physical distortion so as to split the energy levels apart. JT distortions are thought to play a key role in the electronic properties of the alkali metal ($A_3C_{60}$) fullerides which range from insulating to metallic (2) and even high-temperature superconductivity (3).

There are technological considerations as well. $C_{60}$ is an ideal building block for molecular devices because electrons can easily be donated to the fullerene cage from other molecules, atoms, and surfaces. In the case of $A_3C_{60}$, about one electron is transferred from each alkali-metal atom that sits in the interstitial sites of a $C_{60}$ crystal or monolayer. So where do these electrons go?

Pure $C_{60}$ is insulating. Its highest occupied molecular orbital (HOMO) is a fivefold degenerate band with a full complement of 10 electrons, whereas the lowest unoccupied molecular orbital (LUMO), some 2 eV above it, is a threefold degenerate band that could hold 6 electrons but is in fact completely empty. $C_{60}$ is therefore a band insulator (see the figure). Additional electrons donated from the alkali-metal atoms are transferred into the LUMO, and on this basis we can intuitively understand why $K_3C_{60}$ is metallic (because it has a half-filled conduction band). Perhaps the more compelling question, then,
Changing the Cofactor Diet of an Enzyme

Andrew D. Ellington and J. J. Bull

Certain molecular processes are fundamental to all free-living organisms. The minimal set of genes necessary for life may be as small as a few hundred, as can be inferred from genome sequence comparisons across diverse organisms (1). Because this minimal set is so fundamental, it would be especially rewarding to understand the requirements for, and constraints on, a minimal metabolism. Understanding these parameters should also provide insights into how metabolism originally evolved. Yet such an endeavor seems fraught with one basic problem: If all life requires an essential function, how can we study life without that function?

On page 499 in this issue, Lunzer et al. (2) addresses a fundamental issue in metabolic evolution and gets around this dilemma. The authors choose a limited but relatively invariant feature of metabolism—biosynthesis of the amino acid leucine. All known forms of life need leucine. Those organisms that synthesize it use an enzyme called isopropylmalate dehydrogenase. In turn, this enzyme uses the coenzyme nicotinamide adenine dinucleotide (NAD\(^+\)) as a hydride acceptor during an oxidative decarboxylation. Not only is the use of NAD\(^+\) by isopropylmalate dehydrogenase found in all three domains of life, but NAD\(^+\) is the only cofactor so far found to be used by this enzyme. We can thus presume that this property of leucine biosynthesis is at least as old as the last common ancestor of modern life.

This invariant use of NAD\(^+\) might be less puzzling were it not that a related tricarboxylic acid cycle enzyme, isocitrate dehydrogenase, uses NAD\(^+\) as a cofactor in some species but uses nicotinamide adenine dinucleotide phosphate (NADP\(^+\)) in others. Why, then, does isopropylmalate dehydrogenase use only NAD\(^+\)? Although there are apparently no extant natural enzymes that could help answer this question, it can nonetheless be addressed by enzyme engineering. Studies of the reaction kinetics and mechanisms of isocitrate dehydrogenase, combined with crystal structures and phylogenetic