Molecular Orbitals Tell the Story
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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$_3$C$_{60}$ 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) fullerides A$_x$C$_{60}$, 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$_x$C$_{60}$, 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$_3$C$_{60}$ is metallic (because it has a half-filled conduction band). Perhaps the more compelling question, then,

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**References**


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is why $K_4C_{60}$ and a host of other $A_vC_{60}$ compounds are not metallic, despite having a partially filled LUMO band.

In fact, the underlying physics of both these compounds is intriguing because their strong interelectron repulsion should outweigh the energy gained by delocalizing the electrons in the crystal, thus driving these compounds to an insulating state. However, in $A_vC_{60}$, the orbital degeneracy of the LUMO lessens this effect by providing multiple hopping channels for an electron to reach a neighboring site (4, 5). $A_vC_{60}$ compounds, it seems, sit quite precariously on the metallic (and superconducting) side of a metal-insulator transition, so why not also $A_2C_{60}$?

The answer almost certainly lies in the lifting of the orbital degeneracy (6) of the LUMO in $A_2C_{60}$ by the JT effect (7). In this case, it is a spontaneous molecular distortion arising from the coupling of degenerate electronic orbitals with certain vibrational modes of the molecule, leading to a lowering of the total energy. In $A_2C_{60}$, the JT distortion splits the LUMO into two lower (and now fully occupied) degenerate levels and an empty level some 0.1 eV higher in energy (see the figure).

The experiment of Wachowiak et al. reveals the story of the JT distortion in monolayer $K_4C_{60}$ as told by the molecular orbitals involved. The researchers use a surface on which both the metallic $K_6C_{60}$ and insulating $K_4C_{60}$ phases exist simultaneously, which allows direct comparison between the two compounds from both topographic and spectroscopic points of view. Wachowiak et al. show clearly the metallic and insulating nature of the molecules directly beneath the STM tip by mapping the local density of states, of both occupied and unoccupied molecular orbitals, and observing the presence or absence of an energy gap at the Fermi level. When imaging the spatial distribution of the frontier molecular orbitals, they observe very different symmetries for the occupied and unoccupied states. This in itself is indicative of a JT distortion, which affects the two states in different ways, in contrast to the nondistorted molecules of the $K_4C_{60}$ phase. However, a very powerful extension of this approach is the incorporation of detailed theoretical calculations of the expected molecular wavefunctions. Although there are three separate $C_{60}^{−}$ distortions consistent with a JT distortion (indistinguishable from an energetic perspective), only one of these was found to be consistent with the observed topographic images of the molecular orbitals. This combination of experiment and theory is becoming increasingly prevalent in many areas of science and has a very important role to play, especially in the study of molecular nanostructures with both imaging and spectroscopic techniques.

The work of Wachowiak et al. was carried out at low temperature, where infrared data for bulk $K_4C_{60}$ have previously suggested a static JT distortion (8). Although structural evidence for the distortion has been observed for fully orientationally ordered $Cs_2C_{60}$ at higher temperatures by neutron diffraction (9), the same cannot be said for $K_4C_{60}$. This has prompted suggestions that at these higher temperatures, molecular orientations in $K_4C_{60}$ are either complex or disordered or that the JT distortion is not static at room temperature but rather exerts a dynamical effect (10). The molecules in the $K_4C_{60}$ monolayers studied by Wachowiak et al. are certainly ordered and the JT distortion is clearly static, but is this driven to a dynamical JT effect at higher temperatures? Clearly, we have reached another question that is best answered at the single-molecule level. Indeed, there are a myriad of questions surrounding molecular interactions and the mechanisms of molecular electronics that need to be addressed. What is also clear is that the molecular orbitals of these and other systems can tell the story at the single-molecule level, and that by combining reliable calculations with high-resolution techniques that can probe these molecular orbitals, we can address many unanswered questions about the fundamental workings of molecular nanostructures.

References

EVOLUTION

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 metabolicism. 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 tricarboxyl 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 mechanism of isocitrate dehydrogenase, combined with crystal structures and phylogenetic

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