

However, previous research had already established that conditional cooperative strategies have an Achilles' heel ("weak stability") (7). They are invadable, through neutral drift, by unconditional cooperators that in turn pave the way for defectors, resulting in boom-and-bust cycles of cooperation and defection. Van Veelen *et al.* show that with increasing likelihood of continued interactions, the probability of this boom-bust scenario also increases, so that while the likelihood of a permanent defection equilibrium decreases, so does the likelihood of permanent cooperation. Thus, repeated interactions tend to facilitate cooperation in general, but require ever higher levels of population structuring (α) to promote permanent cooperation the higher the probability (δ) that individual pairs continue to interact.

Van Veelen *et al.* evaluate the nature of the interaction between two of the best-known routes to cooperation in the Prisoner's Dilemma. The folk theorem of economics emerges as a special case of their model, demonstrating that with no spatial structure cooperative solutions can evolve—albeit temporarily, so long as there is a sufficiently high continuation probability. However, Hamilton's rule (8) from evolutionary biology also emerges as a special case, such that even with zero continuation probability cooperation can still arise, so long as cooperators are sufficiently likely to interact with cooperators. The emergence of Hamilton's rule emphasizes the close link between population structure (represented by α) and kin selection, in which traits are favored because they disproportionately favor others carrying the same trait (9). Moreover, their results highlight the fundamental interrelationship among these seemingly different mechanisms, with conditional cooperation selected for much the same reason as it arises in spatially structured populations—cooperators helping cooperators (10).

What are behavioral biologists to make of their conclusions? All models are simplifications. Van Veelen *et al.*'s model assumes a fixed probability of interacting again, but individuals can often decide to terminate unsatisfactory interactions, and part-

Pathways to cooperation. Common murre (*Uria aalge*) regularly preen their mates, but they also form reciprocal preening associations with their close colony neighbors, highlighting two potential routes to cooperation: direct reciprocity and population structure. In a recent paper, van Veelen *et al.* (4) considered how these two routes to cooperation interact.

ner switching may be at least as important as partner fidelity in promoting cooperation (11). Likewise, the undermining of conditional cooperative strategies by neutral drift can be eradicated if conditional responses are continually favored by the need to recognize individuals who are unable to cooperate (12). The model accounts for conditional cooperation, but while reciprocity is readily demonstrated in experimental games involving humans, evidence for direct reciprocity in the nonhuman world is controversial (13). Van Veelen *et al.* state that human cooperation may be facilitated by "a strong dose of repetition and a pinch of population structure," but precisely the reverse—little repetition and a strong dose of population structure—provides the best opportunity for permanent cooperation. This leads us to wonder what type of cooperation would emerge if interaction rules α and δ were free to evolve under natural selection (14).

The problem of cooperation has now seen so many solutions that its existence can no longer be considered a puzzle. The existing literature can be classified coarsely as top down or bottom up, with the former approach discussing the problem of cooperation in

broad strokes and providing general solutions, and the latter approach taking observations of apparent altruism and providing specific explanations. At least some of these latter examples [e.g., (1)] may be understood on the basis of direct benefit rather than a Prisoner's Dilemma (15). Eventually, theory and observation will meet, and only then will we really know which general explanations apply to the world around us.

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CHEMISTRY

Discriminating Chemical Bonds

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An atomic force microscope equipped with a functionalized tip can map out the electronic and structural properties of individual chemical bonds.

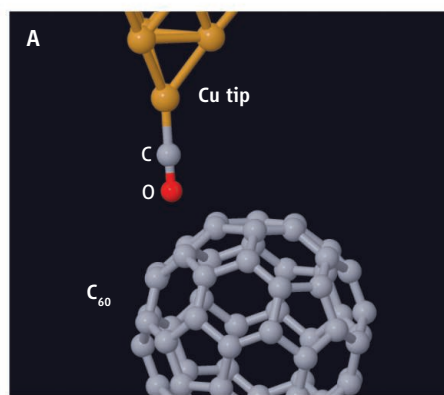
Recently developed operation modes for the atomic force microscope (AFM)—in particular, frequency modulation AFM (FM-AFM) (1)—have made it possible to image, manipulate (2), and chemically identify (3) both conducting and insulating surfaces (4) with atomic-scale resolution. On page 1326 of this issue, Gross *et al.* (5) push the limits of the imaging capabilities of AFM still further by using a functionalized tip—a metal tip with a carbon monoxide (CO) molecule at the apex—to map the subtle differences in charge density

and bond length associated with nonequivalent C-C bonds in three complex molecular systems, and to correlate them with their bond order. The ability to determine fundamental properties of individual chemical bonds could affect many technologically relevant fields such as catalysis, photovoltaics, and molecular electronics.

The strength of the chemical bond between two atoms depends on their chemical environment. The C-C bond strength is progressively reduced in the series acetylene (H-C≡C-H), ethylene (H₂-C=C-H₂), and ethane (H₃-C-C-H₃). This decreasing strength is related to the number of electrons shared by the C atoms (6, 4, and 2, respectively) to form what is referred to as a triple, double, or single C-C bond. Bond lengths correlate

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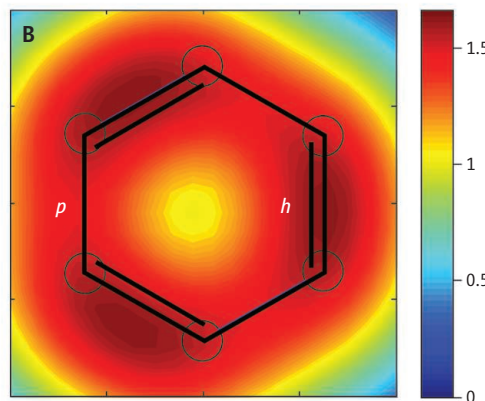
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Forceful discrimination. Gross *et al.* used AFM with a CO-functionalized tip (A) to map the subtle differences in charge density (B) and bond length (C) associated with nonequivalent C-C bonds in a fullerene (C_{60}) molecule and to correlate them with their bond order.

with bond strength: A triple bond is shorter than a double bond, and this is shorter than a single bond. Characterizing the strength of the different bonds in a complex molecule is important in order to predict its geometry, stability, aromaticity, and reactivity. The Pauling bond order (δ), P_b , captures that information in a single number. The bond order of the simplest conjugated molecule, benzene (C_6H_6), is 0.5, reflecting the extra half bond provided by the six additional electrons that are equally shared among the six C-C single bonds defining the hexagonal ring. In more complex molecules, involving hexagons and pentagons, P_b can take any value between 0 (single bond) and 1 (double bond). In a fullerene (C_{60}) molecule, the bonds fusing two hexagons (h) are electron-rich compared to the bonds fusing a pentagon and a hexagon (p), corresponding to $P_h = 0.44$ and $P_p = 0.28$, and leading to differences in bond length of 5%.

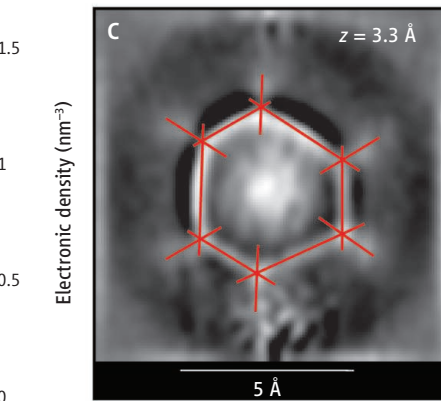
Gross *et al.* show that those subtle differences in electronic charge distribution and length associated with the bond order can be directly measured on individual bonds of a fullerene molecule with the AFM. The key to this achievement is the use of a functionalized tip, in which a closed-shell CO molecule is attached, by the C atom, to the metal tip apex (see the figure). Density functional theory calculations show that the tip reactivity is crucial in determining the nature of the atomic contrast found in the AFM images (7, 8). With chemically inert tips, such as the CO-metal tip, the total tip-sample force is attractive mainly as a result of the long-range van der Waals contribution, but this interaction does not itself yield atomic contrast. Short-range chemical interactions are essentially repulsive (the Pauli repulsion between the overlapping electronic clouds),



and force maxima correspond to the positions with lower electronic density, like the hollow sites at the center of the carbon rings (8). FM-AFM measures the frequency shift, the change of the resonant frequency of the oscillating cantilever where the tip is mounted, due to the tip-sample interaction. Attractive (repulsive) forces produce a negative (positive) frequency shift. Gross *et al.* show that, for moderate tip-sample distances, the frequency shift is sensitive enough to map the differences in charge density associated with the different bond orders of individual bonds: It increases above the h bonds with respect to the p bonds, reflecting the stronger repulsion associated with the larger charge density in the h bond.

Those differences in frequency shift tend to blur when the tip is moved closer to the surface, but Gross *et al.* have found another way to discriminate between these bonds: The h bonds appear shorter relative to the p bonds. The real length difference, just 0.07 \AA , would be at the limit of the AFM lateral resolution, but both bonds appear appreciably longer than they really are in the AFM images, resulting in a difference in apparent bond length 10 times larger. DFT calculations (5) prove that CO tips strike the perfect balance between being noninvasive and sensitive to the tip-sample interaction. When the tip-sample distance is reduced, the CO molecule can tilt in response to the larger repulsive interactions. This tip relaxation leads to an apparent expansion of the molecule in the image (roughly proportional to the local charge density) and the amplification of the subtle bond length differences. These capabilities have been confirmed in two large polycyclic aromatic hydrocarbons that contain bonds of several different bond orders, where AFM resolves differences in bond order down to 0.2 and distinguishes individual bonds that differ only by 0.03 \AA in length.

The ability to map subtle differences in electronic density and length on individual bonds paves the way for a fundamen-



tal understanding of the charge redistribution processes that control electronic transport and chemical reactivity. Defects are crucial to tune the electronic properties of carbon-based materials like graphene, but they also affect the coupling with the local environment, which is critical to integrating them in tomorrow's electronic devices. AFM with CO tips offers the possibility of mapping the structural distortions and the subtle charge modulation predicted for single-atom vacancies and graphene nanoribbons. It has already been shown that a different type of force microscopy, Kelvin probe force microscopy, is able to control and measure the charge state of an individual atom (9) and to map changes in the local contact potential at submolecular resolution using a CO tip (10). Adding the new AFM capability to track small changes in the charge distribution around a bond should make it possible to use metal atoms attached to a molecule to add or remove charges and to identify the specific sites that would become active during a photochemical or electrochemical reaction. Future developments are not restricted to molecular systems. In the long term, one can envision the use of tips functionalized with tailored molecules exposing acidic or basic groups to identify and map the chemical reactivity of active centers in catalytic materials like transition metal and rare-earth oxides.

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