

Photoelectron spectra explain how ammonia solutions become metallic **FREE**

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but instead replaces the problematic gene. Optogenetic treatments, which can restore light sensitivity even when the cause of the degeneration is not known, are currently in clinical trials.

But optogenetic therapy suffers from a major unmet challenge. A healthy retina can detect light over eight orders of magnitude in brightness, from a faintly lit room to a sunny summer day. The microbial proteins used in optogenetics are sensitive only to the brightest end of that range. To see under dimmer conditions, an optogenetic patient must wear video goggles that image the visual scene and amplify its brightness. That strategy works well for someone who's totally blind, but photoreceptor degeneration is a progressive condition that's debilitating long before blindness is complete. For a patient with some remaining vision, the healthy photoreceptors would be overwhelmed by the goggles' bright light.

The new work aims to surmount that hurdle by creating vision at a wavelength that healthy rods and cones can't see. Because the world doesn't look the same in the near-IR as it does in the visible regime, patients would still need to wear goggles to convert incoming visible light to 915 nm. The remaining healthy photoreceptors can't help to process that image—but they also won't be overwhelmed.

Engineering nanovision

Gold nanorods, an essential component of Nelidova and colleagues' near-IR sensors, are no newcomers to biomedical applications. Because of their surface plasmon resonances, metal nanoparticles are exceptionally good at absorbing light and converting it into heat (see the article by Mark Stockman in *PHYSICS TODAY*, February 2011, page 39), and they can be tuned through their size and shape to absorb at a particular desired wavelength. Among their uses is photothermal therapy for cancer, which involves targeting them to a tumor and zapping them with a laser to cook the tumor to death. Although the heat they give off can wreak selective havoc on tissues, the nanoparticles themselves appear to be safe and biocompatible. And they can be injected into the retina in the same surgery as the gene-carrying viruses.

Plasmonic nanorods aren't the only

nanotechnological route to seeing in the near-IR. Last year, Tian Xue and colleagues of the University of Science and Technology of China showed that they could endow mice with near-IR vision using so-called upconversion nanoparticles, whose structure of a core wrapped in an outer shell allows them to absorb light at one wavelength and emit it at a shorter one.³ (For more on upconversion nanoparticles, see the article by Marco Bettinelli, Luis Carlos, and Xiaogang Liu in *PHYSICS TODAY*, September 2015, page 38.) They chemically anchored their nanoparticles to retinal photoreceptors—the mice they used weren't blind—so that when the particles absorbed in the near-IR and emitted in the visible, the light was visually processed in the normal way.

Because Xue and colleagues' approach relies so heavily on the existing retinal structure, their mice could recognize and distinguish simple near-IR spatial patterns. Nelidova and colleagues, so far, have shown only that their mice can detect an undifferentiated near-IR flash. And in seeking to restore vision to degenerated human retinas, they face an additional challenge. The topology of neural connections in the retina is complicated, and it's not clear whether a lost photoreceptor cell can be adequately replaced by a neuron in the same location. As Nelidova notes, "Restoration of high-resolution vision is still many years away."

Another unknown is how long the treatment will last: Is a single injection of genes and nanoparticles good for a lifetime, or does its effectiveness eventually wane? The researchers are hoping for the

former: A subretinal injection is a difficult surgery that's especially challenging to perform more than once in the same eye. Although gene therapy is still a young technology, the coming years will provide a clearer picture of its long-term outcomes in Lebers congenital amaurosis patients and the subjects of optogenetic clinical trials.

As for the nanoparticle half of the sensors, mature retinal cells don't divide, so a single procedure to dose the existing cells with nanoparticles should suffice. But if the particles aren't securely anchored in place, they could be cleared by the body and lost.

To solve those problems, the Basel researchers are working on optimizing their near-IR sensor by tinkering with its parts. Across the animal kingdom, there are many variants of the thermosensitive protein, each of them responsive to a slightly different temperature. Nanoparticles can be tuned in size and shape, and the protein tags and antibodies can also be reengineered. The researchers have tested several of the possible combinations so far, and they plan to explore further. Says Nelidova, "One reassuring thing shown by the experiments is that we can disconnect, reconnect, and exchange sensor components, with predictable final outcomes."

Johanna Miller

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Photoelectron spectra explain how ammonia solutions become metallic

The gradual emergence of delocalized electron states in lithium–ammonia solutions underlies their transition.

Dropping a chunk of sodium into water and watching it explode is a classic high-school chemistry demonstration. The violent reaction is caused by the alkali metal's dissociation into Na⁺ ions and electrons when it enters H₂O. The electrons react with the water to lib-

erate hydrogen atoms, and those quickly pair to form H₂ gas that is ignited by the exothermic reaction.

The same demonstration becomes less incendiary if H₂O is replaced with liquid ammonia, because NH₃ is harder to break apart. Whereas about 1 in every 10⁹

H₂O molecules self-dissociates (roughly 10⁻⁷ moles per liter), only about 1 in 10¹⁷ NH₃ molecules does. Free electrons' brief lifetimes in water—less than a microsecond—make them, and their effects on the molecules around them, difficult to observe. But in ammonia, the formation of H₂ gas is slow enough to form metastable alkali metal–NH₃ solutions. Ammonia solutions can therefore be used to study solvated electrons, which are highly reactive participants in many chemical reactions, including the Birch reduction that was critical for developing synthetic steroids and the first oral contraceptives.

Nuclear magnetic resonance and electron spin resonance have long been used to study alkali metal–NH₃ solutions,¹ but to directly probe their energetics, photoelectron spectroscopy (PES) is the favored technique. It entails bombarding a material with x rays or UV light to eject electrons; the electrons' kinetic energies are then measured to determine their binding energies. Unfortunately, applying PES to alkali metal–NH₃ solutions is difficult. The ultrahigh vacuum needed to give photoelectrons an unimpeded path to the spectrometer causes the volatile liquid ammonia to evaporate almost immediately. Samples must be kept below –33 °C, the temperature at which am-

monia boils, and in a meticulously clean environment to avoid unwanted auxiliary reactions.

Now Tillmann Buttersack (then at IOCB Prague, Czech Academy of Sciences, now at the University of Southern California), Ryan McMullen (USC), Phil Mason (IOCB Prague, CAS), Christian Schewe (Fritz Haber Institute of the Max Planck Society), and coworkers have overcome those challenges by performing PES on alkali metal–NH₃ microjets using lithium, potassium, and sodium.²

Their measurements span a range of concentrations over which the solution's behavior transitions—from electrolytic, in which localized ions carry currents as in salt solutions, to metallic, with extended electron states that facilitate charge transport. The spectrum's evolution points to a gradual change in electronic structure as the dissolved metal concentration increases. Along with simulations, the results suggest that localized electrons coalesce into a system-spanning electron network to cause the metallic transition.

A fine blue color

Alkali metal–NH₃ solutions have been studied for more than 200 years, and much is already known.³ Humphry Davy

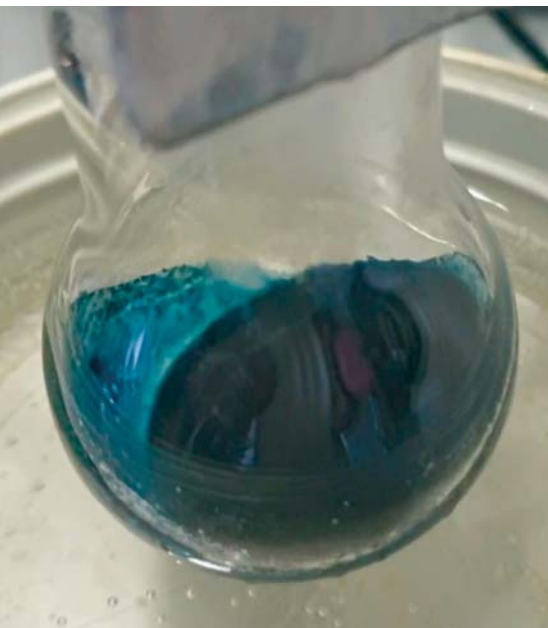


FIGURE 1. ALKALI METAL–AMMONIA SOLUTIONS are a deep blue color at concentrations below about 4 mol percent metal. At higher concentrations their electrons transition from localized to extended states, which causes the solutions to turn bronze and exhibit metallic behavior. (Courtesy of Philip Mason.)

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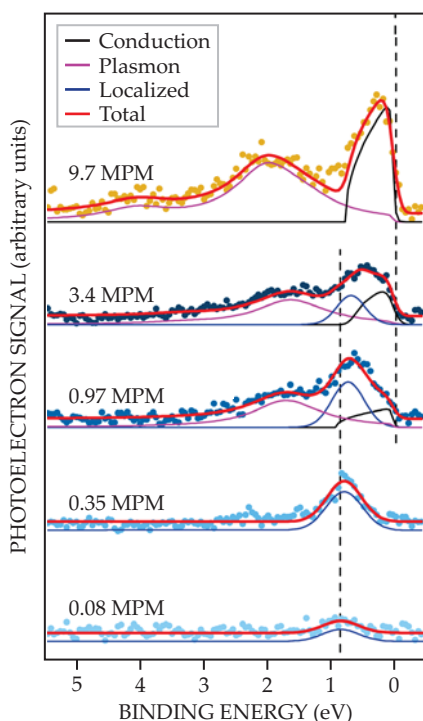


FIGURE 2. PHOTOELECTRON SPECTRA OF LITHIUM-AMMONIA SOLUTIONS

show an evolution from electrolytic to metallic behavior. At low mol percent metal (MPM), dissociated electrons sit in localized cavities surrounded by NH_3 molecules. A single spectrum peak reflects the binding energy associated with those cavities. As the MPM increases, the electrons form extended wavefunctions like those found in metals. Models (solid lines) show that the increasing prevalence of a free-electron conduction band and collective oscillations, or plasmons, account for the spectrum's peaks. (Reprinted from ref. 2, with permission.)

first reported on them in 1807 while trying to prove that potassium was an element rather than a hydride of potash; he observed that the metal was dissolved by gaseous ammonia and produced a blue film. Ammonia having been liquefied in 1823 enabled further experiments, including the discovery of the solution's metal transition more than 50 years later.

Subsequent studies have filled in details. At low concentrations—below a mole fraction of about 10^{-5} , or 10^{-3} mol percent metal (MPM)—electrons and cations from the dissolved metal are isolated in localized cavities surrounded by NH_3 molecules. A conductive electrolytic solution results. The solvated electrons absorb IR

light, and in ammonia that absorption peak bleeds into the visible spectrum and produces the deep blue color shown in figure 1.

Increasing the metal concentration beyond 10^{-3} MPM results in pairing—first between electrons and cations, and then between opposite-spin electrons—which reduces the solution's conductance. By about 0.5 MPM the conductivity reaches a minimum, a feature also seen in simple salt solutions.

Above 1 MPM, however, the ammonia solution's conductivity increases, and around 4 MPM the solution turns bronze (see figure 1). Ammonia is unusual in that it can support high enough solvated electron concentrations to reach that transition. The metallic sheen reflects underlying behavior: Previously localized electrons inhabit extended states like those responsible for conduction in familiar metals; they screen the electric field of incoming visible light to produce a telltale reflectivity. When the solution reaches saturation around 20 MPM its conductance is about half that of mercury; that's noteworthy considering there are four nonconducting ammonia molecules for every solvated electron in the solution.

The research groups of long-standing collaborators Bernd Winter (Fritz Haber Institute of the Max Planck Society), Stephen Bradforth (USC), and Pavel Jungwirth (CAS), all authors on the paper, teamed up to study and help explain the mechanism behind the metallic transition. They collaborated remotely to design and perform PES measurements on metal- NH_3 solutions, with their experimental prototype being assembled in Jungwirth's lab in Prague. But before they could tackle the question at hand, they had to overcome a critical experimental hurdle: keeping the ammonia solutions liquid under experimental conditions for long enough to make measurements.

Jet setters

The collaborators turned to a microjet technique that has been used to apply PES to water, simple alcohols, and even liquid nitrogen and argon. Fast-flowing jets refresh the liquid in the observation window quickly enough to compensate for evaporation. Ammonia is liquid between -77°C and -33°C at atmospheric pressure, so they cooled their samples and

the surrounding equipment to -60°C . But that's not so cold compared to argon, whose boiling point is -186°C . The bigger challenge was making sure the apparatus was impeccably clean: Ammonia is reactive, and any insoluble products could clog the micronozzle. With conditions just right, the ammonia formed a stable liquid jet a few centimeters long.⁴

By the time the researchers reported on pure ammonia jets in 2019, they were already applying the technique to solutions with solvated electrons. As in their previous experiments, they bombarded microjets of the solutions with high-brilliance x rays from the BESSY II synchrotron radiation source.

Figure 2 shows the photoelectron spectra for lithium-ammonia samples at concentrations from 0.08 to 9.7 MPM, spanning the metallic transition. For the lowest concentrations, 0.08 and 0.35 MPM, a single peak corresponds to the energy needed to kick a solvated electron out of its ammonia cage. Then, around 1 MPM—the concentration at which conductivity starts increasing—the spectrum develops a more complicated form. The researchers showed that contributions from two electron populations, those in localized and extended states, explain the change. A Gaussian peak accounts for isolated electrons, and a free-electron gas model accounts for metallic ones. The free-electron gas model, commonly used to describe metals, contributes a conduction band and plasmon resonances.

The fraction of isolated electrons needed to account for the observed spectra decreases with increasing metal concentration. At the highest concentration, 9.7 MPM, the spectrum is entirely described by the free-electron gas model, and the conduction-band peak has the predicted sharp edge at the Fermi energy. A plasmon peak in the visible range accounts for the solution's bronze, rather than silver, appearance. The 9.7 MPM spectrum's shape closely mirrors that of 50–50 sodium-potassium, a more standard liquid metal that the researchers tested for comparison.

Structural shifts

Ab initio molecular dynamics simulations performed by coauthor Ondřej Maršálek, an assistant professor at Charles University in Prague, paint a more detailed molecular picture. He found that

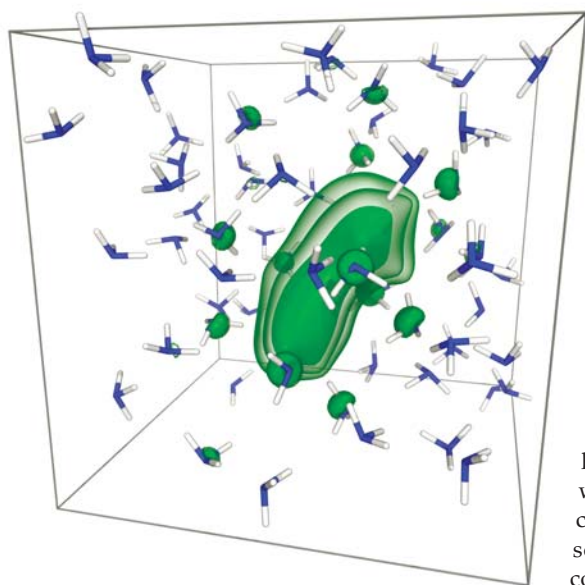


FIGURE 3. MOLECULAR DYNAMICS SIMULATIONS provide details about the size and structure of the cavities that house electrons solvated in ammonia. Spin-paired electrons, shown in green, are surrounded by approximately 12 ammonia molecules (blue and white). Those molecules form cavities about 4.4 Å across; the cavities around unpaired electrons are approximately 3.9 Å. (Courtesy of Tomáš Martinek and Ondřej Maršálek.)

both isolated and spin-paired electrons in solution are surrounded by a diffuse layer of approximately 12 ammonia molecules (see figure 3). The cavities confining solvated electrons in ammonia were about 3.9 Å in diameter for a single electron and 4.4 Å for paired electrons.

One simple explanation for the onset of metallic behavior is the Mott criterion, which says that metallic conduction should arise when the average distance between the diffuse solvated electrons is less than approximately four times their extent. At 1 MPM, that distance would be about 4 Å. But that picture is too simplistic—such a transition would be abrupt, whereas the Li-NH₃ spectrum evolves gradually. Unfortunately, there isn't another system with an analogous transition to guide the researchers' thinking. Based on their data, they suspect that coalescence of electron cavities into a continuous network underlies the transition to a metallic state. But at the moment that's just a guess.

Pinning down what's really happening in the transition will require improved

simulations. Maršálek had already upgraded to a more accurate electron density functional and a more extensive set of basis functions compared with his earlier studies of water.⁵ Both were necessary to reproduce the known bound state, which is more diffuse in ammonia than water, but they increased the simulation time by up to three orders of magnitude.

Extending simulations to higher metal concentrations will require Maršálek to include cations, which he reasonably neglected at low concentrations. The main challenge is that ammonia solu-

tions are dynamic and disordered. Fully simulating the diffuse electrons, metal cations, and solvent molecules in all their possible configurations requires a lot of sampling, which makes the already expensive computation even more daunting.

Despite its challenges, the inclusion of cations is an important next step. At increasing metal concentrations, they're likely to be important to the formation, structure, and dynamics of an electron network. The researchers suspect that, like the atomic lattice in crystalline conductors, the cations provide the background potential for extended electron states.

Acquiring complementary experimental information on electronic structures throughout the metallic transition would require neutron or x-ray scattering, and the collaboration's experimentalists hope to attempt those measurements. But that doesn't mean they're done with PES; studies on highly concentrated electrons in water are already in the pipeline.

Christine Middleton

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