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Spotlights on Recent *JACS* Publications

VERTICAL BINDING ENERGY OF QUASI-FREE ELECTRONS IN ICE NAILED WITH FEMTOSECOND PROBING

The property of water as an effective solvent depends on the polarity of the water molecules and is reflected in its ability to solvate excess electrons, which play a vital role in many chemical reactions. The quasi-free electrons move through the conduction band of water very quickly before becoming trapped by clusters of water molecules. However, determination of the vertical binding energy (VBE) of these electrons has proven challenging because the trapping happens in a few femtoseconds.

Using femtosecond time-resolved photoelectron spectroscopy, researchers led by Julia Stähler have succeeded in following the energy trajectory of electrons when injected into a layer of amorphous solid water (ASW) from a copper template by an ultrashort laser pulse (DOI: 10.1021/ja511571y). A subsequent, second laser pulse takes a snapshot by ejecting the electron from the ASW layer and measuring its VBE. By variation of the time delay between the laser pulses, the rapid passage of the excess electron through the ASW is filmed in real time.

The researchers find that the electron nearly instantaneously reaches the bottom of the conduction band and is trapped by pre-existing cages of water molecules within only 22 fs, before they can rearrange to adjust to the extra negative charge. When snatched by the water molecules, the electron increases its VBE from 0.8 to 1.4 eV.

Alexander Hellemans

SYNTHETIC RECEPTOR HOLDS ON TIGHT TO SHORT PEPTIDE SEQUENCE

Chemists have long sought to create synthetic structures that mimic an antibody's amazing ability to recognize peptide motifs with enormous affinity and specificity, but efforts to date have been met with limited success. Now, Adam Urbach and co-workers from Trinity University in San Antonio, Texas, report a supramolecular structure that binds to a short peptide sequence in aqueous solution as tightly and specifically as an antibody (DOI: 10.1021/jacs.5b00718).

The researchers assess the ability of the organic macrocycle cucurbit[8]uril (Q8) to team up with a fluorescent reporter and detect binding to a library of more than 100 three-amino-acid peptide sequences. Previous reports had shown that Q8 binds peptides with N-terminal aromatic residues. Here, the team is the first to explore the effects of residues adjacent to N-terminal residues Trp, Phe, and Tyr and to discover that Q8 binds to Tyr-Leu-Ala with an equilibrium dissociation constant, K_d, of 7.2 nM, a significant improvement over synthetic receptors that commonly exhibit K_d values in the micromolar range.

The structure could serve as a more affordable and stable alternative to monoclonal antibodies for applications in biosensing and other biological assays that require the recognition of recombinant proteins.

Christine Herman, Ph.D.

INTERSTITIAL QUASIATOMS: ATOMS (AND MOLECULES) WITHOUT NUCLEI?

Introductory chemistry courses often begin by teaching the basic principle that atoms are the foundation of the chemical world. Atomic nuclei contain protons and neutrons, and electrons in the shells or orbitals interact with other atoms. This basic rule is now expanded by Mao-Sheng Miao and Roald Hoffmann. The team describes interstitial quasiatoms, which lack nuclei and core electrons, yet show all the chemical features of standard atoms (DOI: 10.1021/jacs.5b00242).

Density functional theory calculations are carried out to further explore electrides, some known, some hypothetical—essentially ionic compounds where the anion is an electron—under high-pressure conditions. The authors illustrate that electrons in the space confined between atoms in a high-pressure environment occupy quantized states similar to s, p, and d orbitals. These so-called interstitial quasiatoms can, so far only in theory, form bonds with each other or with neighboring atoms through ionic, covalent, and even metallic bonding.

This detailed study establishes and extends the scope of high-pressure electrides. The presence of anion-like pockets of electrons in these is known; their potential to form quasimolecular units is new.

Hui Jin, Ph.D.

HOW TWO ENZYMATIC ROADS DIVERGE INTO SEPARATE NATURAL PRODUCTS

Wilfred A. van der Donk and colleagues have determined how two highly similar enzymes generate different natural products from the same substrate (DOI: 10.1021/jacs.5b00282).

Two nonheme iron oxygenases, 2-hydroxyethylphosphonate dioxygenase (HEPD) and methylphosphonate synthase (MPnS), act on the same phosphonate substrate and have similar sequences, but produce two distinct products. In soil-dwelling bacteria, HEPD converts 2-hydroxyethylphosphonate (2-HEP) to hydroxymethylphosphonate and formate during biosynthesis of an herbicide. In contrast, in archaea found in the ocean, MPnS converts 2-HEP to methylphosphonate.

Biochemists want to know how such similar enzymes can behave so differently. To investigate this question, van der Donk and co-workers create a mutant form of HEPD by varying an amino acid at a position where the enzyme's sequence varies from that of its cousin MPnS.

The mutant enzyme shows the activity of both catalysts: presented with the substrate, it produces similar amounts of hydroxymethylphosphonate and methylphosphonate. By reacting the non-natural enzyme with a deuterium-labeled substrate, the team concludes that the two wild-type enzymes have similar mechanisms, and that a methylphosphonate radical acts as a branch point for product formation. The work could help clarify our understanding of the biosynthetic mechanism of these and other natural products.

Deirdre Lockwood, Ph.D.

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FLUORINE NMR TELLS MIRROR-IMAGE MOLECULES APART

Enantiomers—mirror-image molecules—are the same in many ways, yet biology and chemistry tend to focus on the differences. For example, enzymes typically recognize one enantiomer and not the other, which may determine whether a drug that targets an enzyme actually works. Differentiating between enantiomers is critical for synthetic, medicinal, and biological chemistry; unfortunately, existing methods for doing so are slow or technically demanding. Using fluorine-19 NMR spectroscopy, Yanchuan Zhao and Timothy Swager have developed a simple and rapid approach to detect enantiomers in a sample using a chiral-sensing molecule (DOI: 10.1021/jacs.5b00556).

The researchers have designed the chiral sensor around an atom of palladium, a metal that binds reversibly to amines, with a fluorine atom on each arm of the sensor. These fluorine atoms are sensitive to subtle changes in their chemical environment, which show up as chemical shift differences in the NMR spectra. The spectra of the sensor mixed with amine-containing enantiomers reveal two distinct peaks, one for each enantiomer, with the relative intensities of the peaks corresponding to the ratio of enantiomers. The researchers demonstrate the utility of this method by simultaneously differentiating between 12 chiral amines (6 pairs of enantiomers), each of which gives a distinct NMR peak. The method also has the potential to resolve enantiomers that are difficult to separate by HPLC.

Erika Gebel Berg, Ph.D.

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