Liquid helium offers a fascinating new way to make charged molecules

October 24 2014

A collaboration between researchers at the Universities of Leicester and Innsbruck has developed a completely new way of forming charged molecules which offers tremendous potential for new areas of chemical research.

Professor Andrew Ellis from our Department of Chemistry has been working for several years with colleagues at the Institute of Ion Physics in Austria on exploring the chemistry of molecules inside liquid helium. The team's latest and most startling discovery is that helium atoms can acquire an excess negative charge which enables them to become aggressive new chemical reagents.

Helium is a famously unreactive gas but when cooled to just above absolute zero it becomes a superfluid, a strange form of liquid. (Among other bizarre properties, liquid helium can flow upwards because it has zero viscosity and its capillary action is stronger than gravity.) The Anglo-Austrian team manufacture droplets of superfluid liquid helium by subjecting helium gas to a combination of high pressure and low temperature and then force it through a pinhole just 5 µm in diameter into a vacuum chamber. These droplets provide a controlled environment into which molecules can be added to study chemistry.

The molecules in this case were fullerenes, a class of large carbon molecules, named after their geometrical similarity to the geodesic spheres developed by architect Buckminster Fuller in the 1950s. The droplets of helium were passed through a cell containing C60 or C70 fullerenes and the resultant mixture was hit by an electron beam of energy between 0 and 150 eV.

What Professor Ellis and his colleagues discovered was that clusters of five or more fullerene molecules became dianions (gained a double negative charge) when targeted by a beam of about 22 eV. Dianions are not uncommon in chemistry but they are normally very unstable and short-lived outside of common chemical solutions (such as water). The creation of relatively stable fullerene dianions in liquid helium opens up a whole new research area for chemists.

So how have these dianions come about? Adding two electrons sequentially to something is difficult because of Coulomb's Law: the negative charge of the first electron will tend to repel the second electron. What has evidently happened is that two electrons have attached themselves to a fullerene molecule simultaneously. The key question is where do these two electrons come from and why don't they repel each other?

The answer seems to lie with helium. Helium atoms have two electrons in their natural, neutral state, their negative charge being balanced by two positively charged protons. The first orbit or shell around an atomic nucleus can only hold two electrons, which is why helium is generally disinterested in reacting with anything.

However, in these new experiments an electron beam with the right energy excites one of these electrons, causing it jump up to the next orbit where it is joined by an electron from the beam, creating an anion of helium. There are now two electrons in large orbits around the helium nucleus which makes this helium anion very reactive. When a suitably sized target, such as a clump of fullerene molecules, presents itself the two outer electrons jump ship, ending up on the fullerene. This pairing of two electrons which would normally repel each other is most likely aided by the very low temperature (0.4 K) inside the helium droplets and has echoes of the behaviour of electron pairs in superconductors.

Professor Ellis said: "Nothing like this has been observed before and the idea of helium as an electron donor is something completely new. This is really just the beginning of a new branch of chemistry and our research team is now exploring how other chemical processes might be influenced by this remarkable chemical reagent."

The paper 'Formation of Dianions in Helium Droplets' by Mauracher at al has been published in the international journal *Angewandte Chemie*.

More information: "Formation of Dianions in Helium Nanodroplets." *Angew Chem Int Ed Engl*. 2014 Oct 8. DOI: 10.1002/anie.201408172. [Epub ahead of print]

Provided by University of Leicester