Exotic structure of xenon difluoride at high pressure

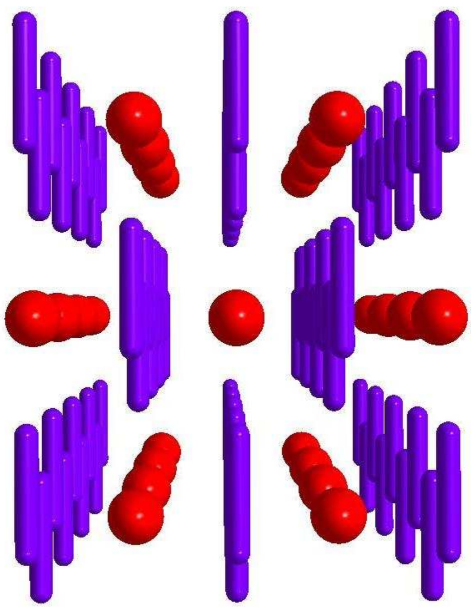
Scientist from the University of Warsaw and Cornell University have predicted unusual behavior in one of the simplest noble gas compounds – xenon difluoride. The results of their research, published in the latest issue of Inorganic Chemistry, hint that that this covalently bound compound may become an ionic crystal when subject to a pressure of two million atmospheres.

For more than six decades after their discovery at the end of the 19th century the noble gases (helium, neon, argon, krypton, xenon and radon) had been considered as unable to form stable, neutral chemical compounds. This prejudice was refuted in 1962 by the first synthesis of a compound of xenon. One of the most stable compounds of xenon is its difluoride (XeF_2), an exotic compound, yet one that has found a use as an etchant in the production of silicon semiconductors.

Dominik Kurzydlowski and Wojciech Grochala from the University of Warsaw together with Roald Hoffmann from Cornell University have conducted a computer simulation in which XeF_2 has been subject to a pressure of two million atmospheres (200 GPa). The original aim of their research was to reexamine and extend to higher pressure experimental data concerning the high-pressure behavior of this compound reported in the July 2010 issue of *Nature Chemistry* by researchers from Washington State University.

During the elegant experiment xenon difluoride was gradually squeezed to a pressure of one million atmospheres. The data collected indicated that the structure of this compound is drastically altered upon compression. “The reported structural changes on compression bothered us, from a chemical point of view” – says Roald Hoffmann.

Computer simulations, far less costly than high-pressure experiments, indicated that the experimentalists may have misinterpreted the data in an experiment that is not easy. “As a result of a careful comparison of our theoretical results with those obtained experimentally, we were able to suggest where the original interpretation of the experimental data might have gone astray” – explains Dominik Kurzydlowski, a Ph. D. student of Grochala, and adds – “but the most interesting things happened when we simulated the behavior of XeF_2 at a pressure of two million atmospheres, greater than that studied experimentally”.



The high-pressure ionic structure of XeF_2. Violet sticks mark XeF^+ cations, red balls F^- anions.

It turned out that at such compression xenon difluoride forms a crystal containing XeF^+ cations and F^- anions. “At ambient pressure XeF_2 is a linear molecule with two covalent Xe-F bonds. We found that when you squeeze it sufficiently hard it chooses to sacrifice one of its bonds and forms an ionic structure. This enables the atoms to pack better and therefore lower free energy” – says Grochala. This unusual transition is the first one reported for a noble gas compound. “All this shows us how much the high-pressure chemistry of compounds differs from what we know from the ambient pressure world” – concludes Hoffmann.

The article *Freezing in resonance structure for better packing: XeF_2 becomes $(XeF^+)(F^-)$ at large compression* can be found on the *Inorganic Chemistry* web page or as dx.doi.org/10.1021/ic200371a.