Getting the Jump on Superacids

▲ *Michael Klein, Hepburn Professor of Physical Science, University of Pennsylvania, and winner of the 1999 Rahman Prize for Computational Physics.*

They don't come from the planet Krypton or leap tall buildings, but it's not a big stretch to think of superacids as chemical superheroes. Since George Olah's work in the 1960s, which led to the 1994 Nobel Prize in Chemistry, these fascinating compounds have become an essential tool of the chemical industry. Their powerful ability to react with and break down raw petroleum brings us such products as high-strength plastics and lead-free, high-octane gas. Exotic processes like coal gasification are unthinkable without superacids.

"Hundreds of thousands of tons of this material are used in the chemical industry on a routine basis," says Michael Klein, Hepburn Professor of Physical Science at the University of Pennsylvania and director of Penn's Center for Molecular Modeling. "Yet they're mysterious. Why do different superacids have different strength? How does a superacid actually work at the atomistic level?"

Superacids aren't well understood in large part because they are what they are—extremely strong acids. By the accepted definition, superacid means stronger than 100 percent sulfuric acid; many are a billion or more times stronger than that. "They are very toxic, very volatile," says Klein's collaborator, post-doctoral fellow Dongsup Kim, "and it's difficult to do experiments."

Using PSC's CRAY T3E, Klein and Kim provided new insight into the relation between the molecular structure of superacids and acid strength, and produced the first detailed picture of a fundamental superacid property called proton jumping.

Naked Protons

Acids are defined by their ability to "protonate" bases—that is, to donate protons. The key chemical species is the hydrogen nucleus, naked H+, stripped of its single electron. In liquids, the naked proton is always bound with either the acid or solvent. Free protons exist only in the gas phase, one reason why experiments have focused there, yielding information not available experimentally with liquids.

"Chemistry for 50 or 60 years has had a diversion into the gas phase," says Klein. "Real chemistry happens in solutions, but we couldn't do studies of liquids 25 years ago, because the computing hardware wasn't capable enough, and we didn't have the methods." Today's computational approaches, however, open a window closed to experiment, and Klein and Kim set out to fill in some of the blanks.

Experiments with one of the superacids, boric trifluoride in hydrogen fluoride (BF_3/HF) indicated a feeble, electrostatic attraction between BF_3 and HF in the gas phase—called a van der Waals attraction. One might expect to see a stronger bond, a chemical bond in which the fluorine atom from HF shares electrons with the boron of BF_3, yielding a BF_4- ion and a naked proton. And this posed a question: If these molecules don't react, why do they form a superacid in solution?

Kim and Klein confirmed the experiment and also showed a more complex picture. With a single HF, there's a weak attraction between BF_3 and HF. With more HF molecules, however, the picture changes. With four HFs, the intermolecular distance decreases, and a chemical bond forms, induced by a ring structure of HF molecules, bound together by hydrogen bonds, that stabilizes the BF_4- ion. With six and seven HFs, the ring architecture is further secured by hydrogen bonds, leading to H_2F+ like structures, suggesting that this protonated HF is a key to superacids. "You need to have a solvent shell of neighbors," says Klein. "That's why the reaction takes place in the liquid."

▼ **Superacid Clusters**
In interaction with a single HF, BF_3 is weakly attracted, as indicated by the bond length (in Angstroms). With four HF molecules, however, a ring structure forms with hydrogen bonds between some of the H (blue) and F (green) molecules. This stabilizes and increases interaction strength between B (red) and the added F atom, as indicated by the shortened bond length. With six and seven HFs, an H_2F+ like structure (shading) further stabilizes the cluster.

2.439

1.768

1.522
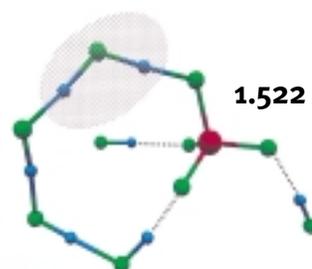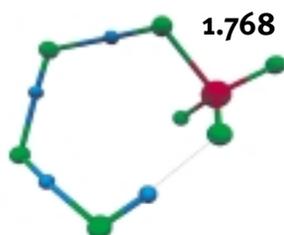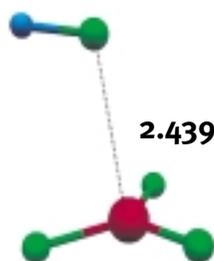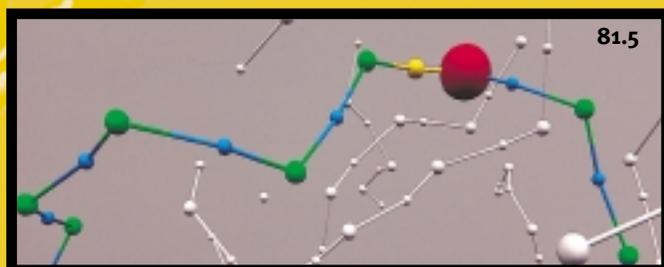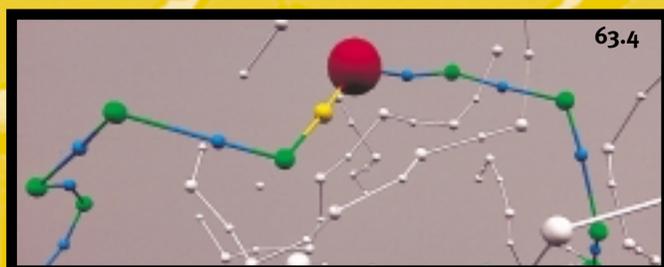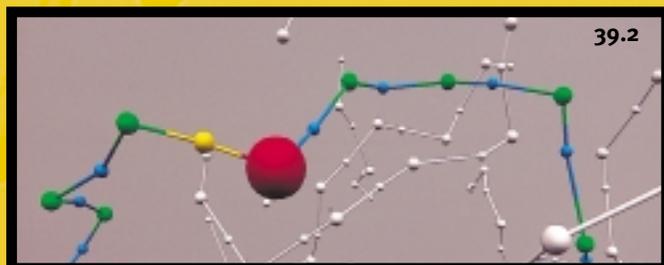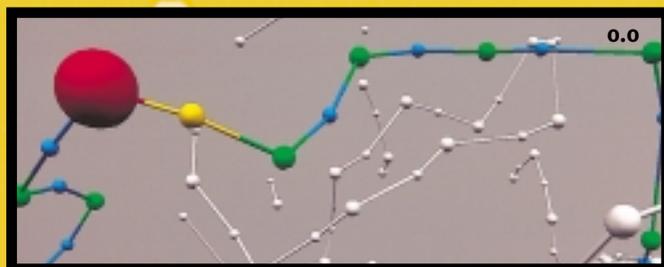
◄ **Proton Leapfrog**
An excess proton (yellow) in solution with 54 HF molecules attaches to a fluorine atom (red) in a pre-existing HF chain (blue and green). These two atoms stay next to each other as they jump down the chain. Time is shown in femtoseconds (a billionth of a millionth of a second). The excess proton and its fluorine partner travel across three bonds in only 81.5 femtoseconds.

[Computation Opens a Window Closed to Experiment]

How Protons Jump

A quantum approach called ab initio molecular dynamics allowed Klein and Kim to delve further into superacids. Ab initio means from first principles or from the beginning, without empirical data. Input to the calculation is solely the atomic numbers of the molecules. It's a computationally intense method, made possible by recent advances in numerical approaches to quantum theory, and it can produce detailed pictures of how molecular structure evolves.

With this approach, the researchers looked at how protons move in superacids. The strongest superacid is antimony pentafluoride in hydrogen fluoride (SbF_5/HF), and experiments have shown that these solutions conduct electricity better than can be accounted for by ionic diffusion, the normal process by which electrons in solution roam from ion to ion.

A plausible scenario, says Kim, arises from the reaction between SbF_5 and HF. When the SbF_5 becomes fluorinated to form an SbF_6^- ion, the free H+ can move into an HF chain, which becomes a pathway for the proton to jump from bond to bond like molecular leapfrog. Chemists have postulated that this "proton jump" scenario underlies the abnormal conductivity and other properties of SbF_5/HF. Using 64 CRAY T3E processors, it took a week of computing to simulate four picoseconds (four million-millionths of a second) of this game of proton leapfrog. The results offer the first detailed picture of proton jumping.

More information:
http://www.psc.edu/science/klein2000.html