

HF vapor



MARTIN A. SUHM
LABORATORIUM FÜR PHYSIKALISCHE CHEMIE
ETH ZÜRICH

HF vapor

The Latsis Foundation and the ETH research commission are kindly giving me the opportunity to present our work on hydrogen fluoride vapor. I will try to do this in simple, general terms and refer to the October 1995 volume of *Berichte der Bunsengesellschaft - Physical Chemistry* (p. 1159-1167) for a more detailed account.

Hydrogen fluoride (HF) is a small molecule consisting of a fluorine atom and a hydrogen atom, bound together by a very strong chemical bond. This bond can be visualized by a spring, since the two atoms vibrate against each other (see figure). Among the interesting properties of this molecule, two should be highlighted:

i) HF is probably the simplest representative of a molecule capable of hydrogen bonding. This means that the hydrogen atom in HF has the tendency to look out for another molecule to which it can bind (see figure). Such a hydrogen bond is much weaker than a chemical bond, but it is quite directional. It has just the right strength to be broken and formed easily at normal temperatures. Nature exploits this situation quite heavily in proteins, sugars and nucleic acids. Without hydrogen bonds, we would not be here as living beings. By studying hydrogen bonding in a simple prototype such as HF, we can get insights into this fundamental design element of nature.

ii) From an engineering viewpoint, the vapor phase of HF has some astonishing properties. Vapors are commonly used to store and transport heat in engines, power plants, or chemical reactors. HF vapor can do that about ten times better than any other vapor phase we know. It would be useful to have a qualitative and quantitative understanding of these outstanding properties which are intimately related to the phenomenon of hydrogen bonding.

While a normal vapor consists of single, well-separated molecules, HF vapor is - to large extent - composed of aggregates of such molecules. A typical snapshot will reveal aggregates of 2-8 HF units besides single HF molecules. The connectivity in these aggregates is one-dimensional, (...FH...FH...FH...). As the resulting head-to-tail chains are quite floppy, the larger ones can close to rings (see figure) without effort and thereby achieve an optimal energetic arrangement where each HF molecule happily binds to two neighbours. The equilibrium between these aggregates is very dynamic, with rapid exchange and rearrangement processes.

In order to understand how and why this exceptional aggregation occurs in HF vapor, we have pursued a combined experimental and theoretical approach.

Infrared spectroscopy in supersonic jets

Among the various techniques which can be used to study hydrogen bonding, infrared spectroscopy is probably the most powerful. In this technique, electromagnetic radiation (invisible to our eyes but sensible as heat) is sent through the vapor. If the frequency of the radiation waves matches the frequency of a molecular vibration, it will be absorbed. If we excite a strong spring of the aggregate, the aggregate may even fall apart after the vibrational heat has flown into the weaker bonds. In any case, the absorption signals can tell a lot about the motion in such aggregates. Unfortunately, the signals are blurred due to the intrinsic heat content of the aggregates - the bonds already vibrate heavily before we irradiate them. Hence, they have to be calmed down or cooled prior to their investigation. This can be done by expanding the vapor through a tiny hole into the vacuum. The resulting jet of molecules and their aggregates achieves supersonic velocities and is cooled drastically. By developing and using

techniques based on this principle, we have succeeded in experimentally characterizing the aggregates which are found in HF vapor in terms of their structure, energetics and dynamics. It turns out that aggregates composed of 5 HF units (see figure) play an important and previously overlooked role together with aggregates consisting of 6, 7, and 4 molecules. For the smallest ring aggregate built of 3 monomer units (see figure), we were also able to study in detail the process of ring opening on a timescale of 0.0000000004 seconds after absorption of radiation. If HF vapor is expanded sufficiently, it consists mainly of single molecules and hydrogen-bonded pairs. These pairs or HF dimers are at the doorway of our understanding of hydrogen-bonding and have therefore been studied in particular detail.

Hydrogen bonding in HF aggregates

The interaction between HF molecules in a large aggregate depends on all details of the structure, i.e. it is a complicated function of many variables such as bond lengths and bond angles. In a way, this problem is related to the problem which a sociologist faces when studying interactions in a large group of people. In both situations, the best strategy is to split up the problem. First, the sociologist will have to study the individuals (i.e. HF molecules) in depths. In our case, this is straightforward due to the simplicity of the HF molecule. The next and most important step involves the study of pair interactions, as they are reflected directly in the properties of HF dimer. This provides a very sizeable challenge for modern quantum theory, since the interactions between HF molecules involve some subtle aspects. Therefore, it proved to be necessary to adjust the theoretical results, guided by the experimental results from infrared spectroscopy.

At this stage it is tempting to stop, both in sociology and in hydrogen bonding, and to reduce the interactions in an aggregate of arbitrary

size to the sum of all pair interactions. But we all know that this is an oversimplification. The relationship between three people is more than the sum of all three pair relationships. There is a three-body contribution on top. It is a lot harder to investigate, but can be quite sizeable. For more than three people, there can be more-than-three-body interactions, and a typical soccer game indicates that they cannot be neglected in sociology. Fortunately, we could show that hydrogen bonding is somewhat better behaved. While we have found a very significant three-body contribution to hydrogen-bonding, the four- and higher-body influence is practically negligible in HF. An important effect of the three-body interaction is to discourage branching of the hydrogen-bonded chains. An HF molecule is essentially happy with one partner molecule bound to the hydrogen and one to the fluorine. Of course, the details of these forces are quite complex, but we have succeeded in characterizing them in terms of mathematical expressions, using also some new techniques.

Hydrogen bond dynamics

Once we know the detailed forces between HF molecules, we can study their motion in the aggregates. Due to the laws of quantum mechanics, motion is an intrinsic property of molecules, persisting even at the lowest achievable temperature of zero Kelvin. This so-called zero-point motion is particularly pronounced for hydrogen bonds and we have developed techniques for its accurate computation. These methods are called quantum Monte Carlo methods, because they consist of a simple game of chance. We let the computer make a random decision for an atomic move, and then we check whether this move was a good one or a bad one. By using such techniques, we can learn a lot about motion in hydrogen bonded aggregates. We can learn about bond breaking and forming, about ring opening, about some funny somersaults which the molecules turn, etc. And most importantly, we learn about the energy which it costs

to do all this. Among our findings, there are also some puzzling ones. For example, we find for certain hydrogen bond springs, that they vibrate more quickly when one increases the mass of the molecules. This is completely against everyday experience with springs, but it can be understood and is quite typical for hydrogen bond springs.

Putting things together and getting explanations

By combining our knowledge of the forces, the motions and the spectra of HF aggregates, a unified microscopic picture is obtained. Via the formalism of statistical thermodynamics, we can predict macroscopic properties such as heat storage and transport phenomena of HF vapor. We find that our predictions match nicely with measurements of these quantities. This means that we are on the right track, that we do not miss out anything important.

We can now understand why HF vapor has these outstanding properties. HF ring aggregates are happy micro-societies in which all binding needs are essentially satisfied. The hydrogen bonds are strong so that aggregates made of 5-7 molecules withstand the natural tendency for disorder quite successfully up to high temperatures and down to low pressures. The aggregates can transport and store a lot of heat, hidden in their hydrogen bonds. No other molecule can form saturated micro-societies of such size and extent in the vapor. The most important reason for this has to do with a diffuse, non-directional force between molecules, a kind of general stickiness called the London dispersion force. This London force is superimposed on the directional hydrogen bond force. It is roughly proportional to the square of the size of a molecule and therefore particularly small for HF. When other, larger molecules aggregate, they prefer to do it more completely due to such dispersion forces or due to additional hydrogen bond valences. As a result, vapor compression immediately leads to condensation, i. e. infinite aggregation, rather

than halting at intermediate aggregate sizes. HF molecules have more of a family sense than other molecules.

The work which I have presented is also family work. Many people have helped me in getting the pieces of this story together. Professor Martin Quack has initiated the project and provided an excellent support and framework which made this effort possible. Dr. Katharina von Puttkamer (now married Al-Shamery) has contributed importantly in the early stages of our work. Dr. Ulrich Schmitt and Dr. Hans Hollenstein have helped with the experiments, Dr. Jürgen Stohner, Dr. David Luckhaus and others with the theory. In the group of Prof. David Nesbitt in Boulder/Colorado, I have been given the chance to verify a crucial hypothesis. Special thanks go to my own family - my wife Andrea and our son Patrick - for providing an invaluable counterpoise to science.

Finally, I wish to thank the Latsis Foundation for awarding a prize to this work and for organizing this afternoon. Thank you, ladies and gentlemen, for your attention.

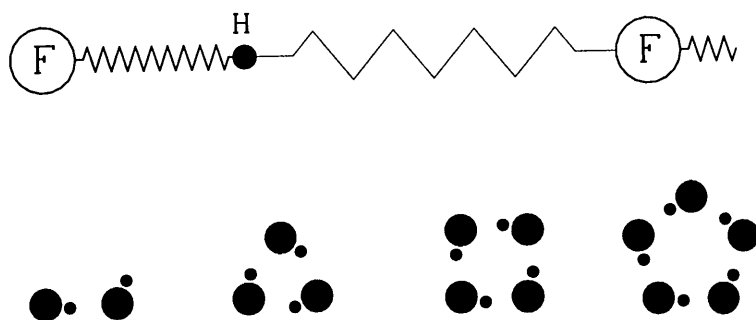


Illustration of the FH chemical bond and the H...F hydrogen bond with springs (top) and the equilibrium structures for aggregates of 2-5 HFF molecules (bottom).