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IUPAC definition of the hydrogen bond. Terminology and nomenclature

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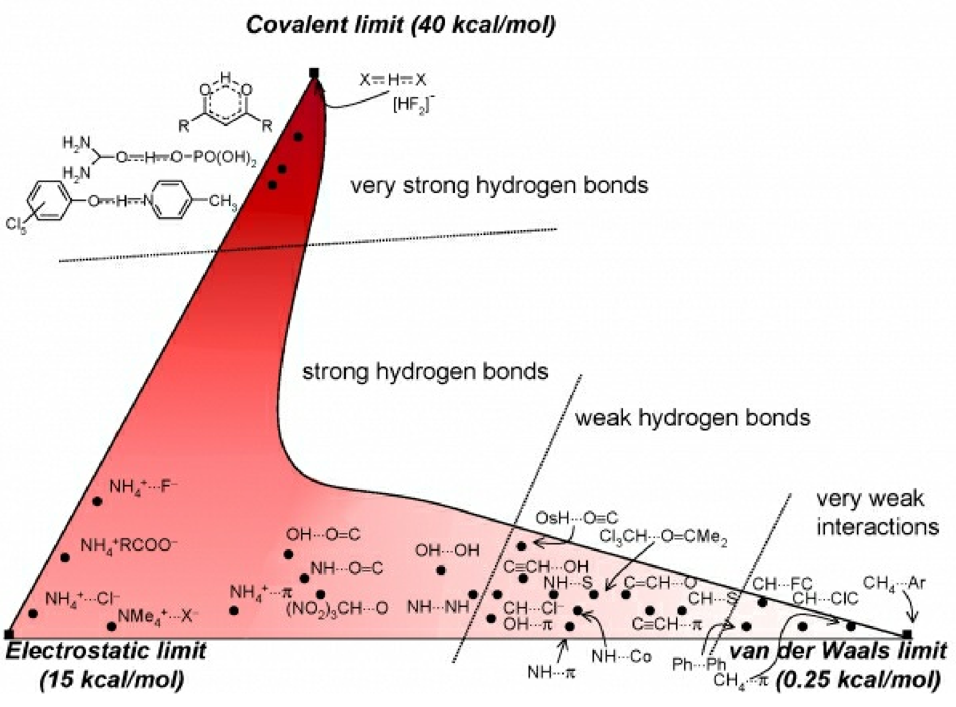
The hydrogen bond is a complex and composite interaction and its definition has undergone evolution over the decades with the appearance of new experimental and computational results. Pauling's original definition is too restrictive and confines itself to strong hydrogen bonds. The Pimentel and McClellan definition is more general and extends the scope of hydrogen bonding to weak donors and acceptors. I was part of an IUPAC committee that recommended in 2011 a definition that attempts to be both accurate and general. Our modern definition states that "The hydrogen bond is an attractive interaction between a hydrogen atom from a molecule or a molecular fragment X-H in which X is more electronegative than H, and an atom or a group of atoms in the same or a different molecule, in which there is evidence of bond formation." The H-atom must be electropositive with respect to X and the accent is on the evidence. The typical hydrogen bond is then represented by X-H...Y-Z where Y-Z is the other "atom or a group of atoms". There are a number of crystallographic, spectroscopic and computational criteria that may be used as evidence of hydrogen bond formation. Generally, such criteria are followed reliably for strong hydrogen bonds. For weak hydrogen bonds, these criteria are followed to a greater or lesser extent and whether or not one terms an interaction X-H...Y-Z as a hydrogen bond depends on a careful evaluation of the particular case. Looser attributes of hydrogen bonds are termed characteristics. There is a gradation in stringency in the application of these criteria and evaluation of these characteristics as the hydrogen bond becomes weaker. These aspects could become controversial in the weakest varieties say C-H...F-C. Hydrogen bonds have been used extensively in crystal engineering. Some aspects of the hydrogen bond definition are more relevant to crystal engineering, for example that they show directional preferences and influence packing modes in crystal structures. The implications of this are that while the crystal packing of a non-hydrogen-bonded solid (say, naphthalene) is largely determined by the principle of close-packing, and each molecule is surrounded by a maximum number of other molecules, there are deviations from this principle in hydrogen-bonded solids to a greater or lesser extent depending upon the strengths of the hydrogen bonds that are involved. Correspondingly, the hydrogen bond geometries are conserved with fidelities that depend on their strengths. Definition of a hydrogen bond is further important because it is the archetype of other similar interactions where another electrophilic species, in lieu of H, is involved. These include the halogen bond, the pnictogen bond and the tetrel bond, all of which are becoming important in crystal engineering.

[1] Arunan. E. et al. (2011) Pure Appl. Chem. 83, 1637-1641.
[2] Desiraju, G. R. (2011) Crystal Growth Des. 11, 896-898.
[3] Desiraju, G. R. (2011) Angew. Chem. Int. Ed. 50, 52-59.



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