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Modern Hydrogen Bonding Theory

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The H-bond was discovered in 1920 by W.M. Latimer and W.H. Rodebush [1] with the collaboration of M.L Huggins [2], three young men working in the laboratory of G.N. Lewis who gave of it a definition based on the Lewis electron-dot formalism which appears to be quite lucid and accurate even in modern terms. By the time that L. Pauling wrote his famous book "The Nature of the Chemical Bond" (1939-1940) [3], the H-bond had received complete systematization within the scheme of the newly developing VB theory, including the distinction between weak electrostatic and strong covalent H-bonds which was successively given VB theoretical dignity by Coulson and Danielsson (1954) [4]. This line of thought was accepted during the 1957 Ljubljana Conference [5] (the first H-bond meeting) and in "The Hydrogen Bond" by Pimentel and McClellan (1960) [6] (the first H-bond book).

This unified approach did not survive the division of sciences in more specialized branches occurred in the post-war period. The accumulation of ever new thermodynamic, spectroscopic and structural data, together with the underlying battle between VB and MO methods, lead to a period of general confusion, summarized in the Hopfinger's (1973) statement "The only one definite fact about H-bonds is that there does not appear to be any definite rules which govern their geometry" [7]. It became clear, however, that the main point of the discussion was centered on the H-bond nature itself, that is on whether the H-bond was electrostatic, covalent, or both, a subject on which the most imaginative positions became allowed.

In 1991, Jeffrey and Saenger published "Hydrogen Bonding in Biological Structures" [8] where, for the first time, the most reliance is placed on the restricted number of accurate neutron structures and, in their absence, on carefully selected X-rays ones. This marks a turning point in H-bond studies: we accept the idea that our previous theories may be in error because based on insufficiently accurate experimental data, suspend temporarily any judgment on them, and start again to collect the widest and most reliable set of H-bond data from which to infer the true nature of the H-bond and then to lay sound foundations for any further theoretical advance. In the last 15 years, this novel data-oriented method of dealing with the H-bond problem has involved many researchers worldwide who, taking advantage of the existing crystallographic (CSD) [9] and thermodynamic (NIST) databases, have produced substantial changes in our way of considering the H-bond phenomenon. These changes will be the object of the present lecture.

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Who is afraid of dynamical scattering?

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"Structural analysis cannot be done by electron diffraction because of the dynamical scattering". "Electron diffraction violates extinctions". "Electron microscopy introduces artifacts." These are just a few of the remarks we regularly hear when discussing with some hardcore X-ray crystallographers. Actually some of the arguments are true! Electron microscopy CAN introduce artifacts and electron diffraction DOES violate extinctions. Nevertheless we will try to convince the audience that electron microscopy is able to do detailed structure analysis by combining information from reciprocal space with information from real space. Also dynamical scattering is no longer an immense problem. When information is available about the exact crystal orientation with respect to the electron beam and the thickness of the sample can be determined independently, modern computers and software packages can now perform dynamical calculations within seconds or minutes. The power of electron diffraction mainly results from the fact that the electron - matter interaction is about 10 000 times stronger than the X-ray - matter interaction. This means that electron diffraction can be obtained from nanometer small areas and therefore it is a local technique, contrary to X-ray diffraction. Actually both techniques are very complementary rather than competitive.

We will consider a few examples to illustrate the power of electron diffraction/microscopy. A first one is Pb₂Fe₂O₅, a perovskite based structure with a complicated incommensurate superstructure. X-ray diffraction only indicates the "probable" presence of a superstructure, while electron diffraction suggests the presence of unusual shear planes in the perovskite structure. High resolution imaging provides evidence of the shear planes, but does not allow to locate the positions of the Pb and Fe cations. In the STEM mode however the Pb positions are clearly identified. A combination of the different techniques allows to propose a structural model for such complicated incommensurate structures. A similar example is Sr₄Fe₆O_{13-x}; a complex structure where different superstructures are formed depending on the exact oxygen content. In Sr_{0.9}Mn₃(O,F)₆ the basic cell is a complex tunnel structure, and the electron diffraction patterns show satellite reflections indicating an incommensurate composite structure with two different repeat periods along the direction of the tunnels, one for the Sr- and one for the octahedral sublattice. This composite aspect passed XRD undetected, which moreover pointed towards tetragonal symmetry. A local investigation with TEM showed that the symmetry is not higher than monoclinic.