

**KN9 Towards the unification of intermolecular forces: The hydrogen bond as a charge-transfer interaction.**

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Since its discovery in 1920, it was evident that the D–H⋯A hydrogen bond (H-bond) could be interpreted in terms of two distinct but complementary theories, that is the Brønsted acid-base or the Lewis acid-base theory. According to the first, the H-bond is a proton transfer (PT) between a proton donor D–H (the Brønsted acid) and a proton acceptor: A (the Brønsted base). According to the second, it becomes an electron exchange between an electron donor: A (the Lewis base) and an electron acceptor D–H (the Lewis acid), which can be written as a D–H←:A  $\sigma^* \leftarrow n$  interaction, a particular member of the class of charge-transfer (CT) or electron donor-acceptor (EDA) interactions introduced and fully classified by Mulliken in the early 1950s [1,2]. This lecture intends to show that both PT and CT visions are suited to give a full representation of the H-bond phenomenon, though with a different focus, the first being particularly appropriate to predict H-bond energies and geometries, and the second to place the H-bond in a wider perspective able to account for all the intermolecular interaction forces occurring in molecular crystals.

The Brønsted theory leads to consider the H-bond as a bimolecular PT reaction transforming D:⋯H–A into D–H⋯:A through the D⋯H⋯A transition state (TS), where what we call H-bond is actually a minimum (or two minima) along this PT pathway adopting a variety of different shapes according to the strength of the H-bond formed. This model represents an easy route to predict the strength of any H-bond in terms of the difference of the donor/acceptor acid/base dissociation constants,  $\Delta pK_a = pK_{AH}(D-H) - pK_{BH^+}(A-H^+)$ , as detailed in the so-called ‘PA/pK<sub>a</sub> slide rule’ method and recently reviewed under the heading ‘the dual H-bond model’ [3–5]. The Lewis theory leads to reconsider all crystal packing forces in terms of CT or EDA interactions. CT complexes were introduced by Mulliken to describe an association between electron donor (D:) and acceptor (A) molecules which is stabilized by the D:⋯A  $\leftrightarrow D^+ \cdots A^-$  covalent-ionic VB resonance and can be equally accounted for in MO terms, where the VB mixing is substituted by a stabilizing second-order perturbation of a ‘donor’ doubly occupied MO (the HOMO) by an ‘acceptor’ unoccupied MO (the LUMO), perturbation which causes a small LUMO←HOMO transfer of charge. Common donors are lone pairs,  $\delta$  bonding pairs and  $d$  bonding pairs ( $n, \sigma, \pi$ ). Common acceptors are vacant AOs, empty  $\sigma^*$  and empty  $\pi^*$  MOs ( $v, \sigma^*, \pi^*$ ). It will be shown that, inside any neutral molecular crystal, all contacts around sum(vdW) can be referred to a well defined type of EDA interaction. This provides us with a novel and particularly easy way of looking at the crystal packing.

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**KN10 Minerals and materials at high pressures: the challenges of complexity.**

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Framework structures, built of relatively rigid atomic clusters, are of central importance to mineralogy, materials science, chemistry and physics. Feldspar, a tetrahedral framework mineral, comprises 60% of the Earth’s crust. The perovskite structure, built of a framework of octahedra, is the most abundant mineral in the Earth and is also a key component of electronics because of the outstanding ferroelectric and relaxor electronic properties of certain compositions. Oxide perovskites are the mostly widely-used substrate material for electronics and perovskite thin films can exhibit exotic electronic and magnetic properties for memory devices. Metal-organic frameworks have recently been the focus of much chemical research to use them for gas storage and the ability to control their catalytic properties by tailored synthesis to incorporate specific functional groups in to the frameworks. Zeolitic frameworks are the basis of the multi-billion euro industry in catalysis of petrochemicals. Critical to all of these applications is the fact that the physical, chemical and thermodynamic properties of frameworks are controlled in large part by the changes in tilting of the relatively rigid polyhedral units that comprise the frameworks. However, the complex topology of many frameworks has, until recently, prevented the direct link being made between the structural topology and the properties. In this talk I will show how improvements in the methods to study the evolution of framework structures at high pressures in combination with modern symmetry analysis, computer simulations and new visualization tools reveals the roles of polyhedral tilting and polyhedral deformation. When the polyhedral tilting is symmetry-breaking, as in perovskites, the tilting and polyhedral deformation can be unambiguously separated and quantified in terms of the symmetry-adapted modes of the structure [1,2,3]. In feldspars the topology of the framework means that the tilts are not symmetry-breaking, although they control the elastic, chemical and physical properties of the material. Nonetheless, the idea of symmetry-breaking tilts of tetrahedra can be adapted to such a case. The decomposition of the variation of the feldspar structure in to four fundamental tilts, and the construction of an exact rigid-body model of the framework can be used [4] to show how the various tilts change the unit-cell parameters, and thus explain the unusual and large 60% elastic anisotropy of the structure. The potential for extension of these methods to other frameworks will be discussed.

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