

Bond valence and bond energy

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We are attempting to build a new kind of molecular mechanics force field based on an expansion of the bond-valence model. The concept of bond valence (a method for estimating bond order from bond length) has been used in many quantitative structure-property models, including the Multisite Complexation (MUSIC) model of Hiemstra and coworkers [1]. One assumption implicit in these models is that bond valence is somehow proportional to the bond energy. However, to date no one has demonstrated the form of this relationship. Are other factors, such as bond character and atomic size, important for determining bond energies?

We have categorized a large number of bonds in small molecules and crystals according to bond valence, bond character (estimated from electronegativity considerations) and bond length, and used these quantities to roughly predict bond dissociation energies.

A consistent, but complex picture emerges from the data. We show that, even for the same bond valence, bond dissociation energies can differ by hundreds of kJ/mol based on their ionic, covalent, or metallic character. Furthermore, covalent bonds less than 2 v.u. are strongly affected by the lone-pair bond-weakening effect identified by Sanders [2]. Bond length plays a more minor role.

Mathematical models of this behaviour will help us parameterize valence-based force fields, by providing initial estimates of bond energies, and model forms.

[1] Hiemstra et al. (1996) *J. Colloid & Interface Sci.* **184**, 680-692. [2] Sanderson (1983) *Polar Covalence*, New York, Academic Press.