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AIM analysis and the form of the bond-valence equation

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Abstract

The bond-valence model (BVM) posits an inverse relationship between bond valence (essentially bond order) and bond length, typically described by either exponential or power-law equations. To assess the value of these forms for describing a wider range of bond lengths than found in crystals, we first assume that the bond critical point density (ρ_b, reported in $e^-/Å^3$) is at least roughly proportional to bond valence. We then calculate ρ_b-distance curves for several diatomic pairs using electronic structure calculations (CCSD/aug-cc-pVQZ) and Atoms-In-Molecules (AIM) analysis. The shapes of these curves cannot be completely described by the standard exponential and power-law forms, but are well described by a three-parameter hybrid of the exponential and power-law forms. The ρ_b-distance curves for covalent bonds tend to exhibit exponential behavior, while metallic bonds exhibit power-law behavior, and ionic bonds tend to exhibit a combination of the two. We next use a suite of both experimental and calculated (B3LYP/Def2-TZVP) molecular structures of oxo-molecules, for which we could infer X-O bond valences of ~1 or ~2 v.u., combined with some crystal structure data, to estimate the curvature of the bond valence-length relationship in the high-valence region. Consistent with the results for the ρ_b-distance curves, the standard forms of the bond valence-length equation become inadequate to describe high-valence bonds as they become more ionic. However, some of these systems demonstrate even higher curvature changes than our three-parameter hybrid form can manage. Therefore, we introduce a four-parameter hybrid form, and discuss possible reasons for the severe curvature. Although the addition of more parameters to the bond valence-length equation comes at a cost in terms of model simplicity and ease of optimization, they will be necessary to make the BVM useful for molecular systems and transition states.

Keywords: Bond valence, AIM, computational modeling, bond order