

Classical and Quantum Mechanical Evaluations of Lattice Energies – Shedding Light on the Covalent Character of Ionic Compounds

Timothy Howarth, Candice Bousquet and Glênisson de Oliveira

Rhode Island College, Physical Sciences Department
600 Mt. Pleasant Ave., Providence, RI 02908

One key measurement of the strength and the ionic character of ionic bonds is the lattice energy. Inorganic chemists will often describe ionic bonds as having high or low covalent character based on whether simple electrostatics is sufficient to properly evaluate lattice energies or other similar thermochemical quantities. When Coulombic interactions fail, it is often assumed that a quantum mechanical treatment of the system is necessary for adequate quantitative evaluations. Obviously, computations based on classical physics are much easier and more tractable than quantum mechanical methods. Qualitatively, several rules and guidelines are used, including Fajan Rules and Pearson's Hard-Soft Acid-Base concept. These are ideas based on polarizabilities, yet no quantitative approach using polarizabilities is commonly used to evaluate ionic compounds with high covalent character. The purpose of this work is to develop easily tractable quantitative models to assess the role of polarizability on lattice energies, and here we report the first steps that have been taken towards that goal. We compare Coulombic interactions with quantum mechanical calculations for one-dimensional arrays of ionic compounds, one with high ionic character and another with significant covalent character, namely sodium chloride and silver chloride.

* This work was supported by NSF grant CHE 0116435, as part of the MERCURY supercomputer consortium, a Title II grant from the US Department of Education, and by the Rhode Island College Faculty Research Funds and Faculty Development Funds