ABSTRACT

STRUCTURE AND BONDING OF TRIATOMIC MOLECULES

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The geometric trends among triatomic *ABC* and tetratomic $(AB)_2$ molecules, with the focus on the Group IIA dihalides, are rationalized using electrostatic polarization models. Two forms of the conventional Rittner-type Polarized Ion (PI) model are evaluated and the influence of monopole-quadrupole contributions is fully assessed.

A Polarized-Core Valence State Atoms-In-Molecules (PVSAM) model is developed as an improvement on the Valence State Atoms-In-Molecules (VSAM) model. The model is formulated in a manner appealing to the notion of configuration mixing and orbital electronegativity equalization and has the general form,

$$\omega = \omega_{att.} + (T/r)e^{-\lambda r},$$

where the attractive part ω_{att} is a sum of Coulomb and dipole polarization terms.

The PVSAM potential function is applied for 74 homonuclear and heteronuclear diatomic molecules. There is a 2-fold improvement over VSAM in the average percentage deviation between the calculated and observed vibration-rotation coupling and anharmonicity constants. In comparison to both the Morse and Rydberg potentials, the improvement in the average errors is over 4-fold for the vibration-rotation coupling constant and 3-fold for the anharmonicity constant. The PVSAM function also out-performs the Rittner ionic potential, for the alkali and alkaline earth halides, with improvement in the average percentage errors in both spectroscopic constants.

It is shown that polarized ion models can indeed reproduce geometric trends for AB_2 and $(AB)_2$ molecules in agreement with experiment. However, the calculated bond angles and force constants do not always compare well with *ab initio* and experimental values. It is found that this is due, to a hitherto unacknowledged extent, to the sensitivity of the PI potential energy function to input parameters, especially polarizabilities, which are not accurately known in many cases. For floppy molecules especially, reaction field influences and quadrupole contributions are decisive.

Contrary to a proposed approach for calculating atoms-in-molecules polarizability, it is found that a potential dependent polarizability leads to a contravention of the law of conservation of energy.

Keywords: Molecular Geometry, Triatomic Molecules, Polarized Ion Model, Valence State.