

Towards an Improved Polarized Valence State Atoms-In-Molecules on Covalent Bonds

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An improved polarizable valence-state-atoms-in-molecules (pVSAM) model has been developed that provides more accurate results when predicting spectroscopic properties (the dimensionless coupling and anharmonicity constants) for group 1 halide diatomic molecules. This new model improves upon the findings of Donald et al. by modifying the polarizing influence of the bond charge on the atomic cores and thus changing the energy contribution of the covalent character of the bond. The change is reflected in the expression of dipole interactions and bond charge fragments, which in the new model is expressed as $W_{cov} = -q^2 / (4\pi\epsilon_0) (7/R + 49(\alpha'_A + \alpha'_B) / (2R^4) - 98\alpha'_A\alpha'_B / R^7)$. It takes into account a full (rather than half) bond charge contribution to the electric field at the atomic centers. Using this new expression, the vibration-rotation coupling constants (F) and anharmonicity constants (G) were calculated for multiple group 1 halides and then compared to both the experimental values and the values calculated by the original pVSAM method. Updated cationic polarizability volumes were also incorporated into both the new and old pVSAM models for better results. These changes, along with newer, more accurate experimental data, produce an increase in the accuracy of the pVSAM method from 6.2% to 5.9% average error for the F values and from 7.0% to 6.7% average error for the G values.