

A Reassessment of the Bond Charge Representation in Polarized Valence State  
Atoms in Molecules (pVSAM) Models

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An improved polarizable valence-state-atoms-in-molecules (pVSAM) model has been developed that more accurately predicts key spectroscopic properties (the dimensionless coupling and anharmonicity constants) for the polar group 1 metal halide diatomic molecules and homonuclear species as well. This new model improves upon previous pVSAM models by modifying the polarizing influence of the bond charge on the atomic cores, significantly alternating the covalent contribution to the bond energy. The change is the revised covalent contribution:  $W_{\text{cov}} = -q^2 / (4\pi\epsilon_0)(7/R + 49(\alpha'_A + \alpha'_B)/(2R^4) - 98\alpha'_A\alpha'_B/R^7)$  takes into account a full (rather than half) bond charge contribution to the electric field at both atomic centers. Using this new expression, the dimensionless vibration-rotation coupling constant (F) and anharmonicity constant (G) obtained for multiple group 1 halides are compared to both the experimental values and the data obtained from our previous pVSAM method. Updated cationic polarizability volumes have been incorporated into both the new and old pVSAM models for better results. These changes, along with newer, more accurate experimental data, produce an overall 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 over dozens of molecules spanning non-polar homonuclear diatomics and extremely polar metal halides.