

Halogen Nuclear Quadrupole Coupling Constants: Comparison of *ab initio* Calculations which include Correlation, with Experiment*

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Ab initio determination of the electric field gradient (EFG) tensors at halogen and other centres enabled determination of the nuclear quadrupole coupling constants (NQCC) for a diverse set of axially symmetric (C_{3v} , $C_{\infty v}$, $D_{\infty h}$ and other symmetries) inorganic and organic molecules, where the heavy elements are Cl, Br, and I with C, Si, Ge, and Sn hydrides. The latter elements are in an approximately tetrahedral environment. The study presents results at a standardised level of calculation, triple-zeta in the valence space (TZV) plus polarisation functions (TZVP) for the equilibrium geometry stage; all-electron MP2 correlation is included in all these studies. f-Orbital exponents were optimised for both Br and I centres in the methanes; the atomic populations of the f-orbital components are very small for the Br- and I-atoms, confirming their role as polarisation functions rather than having any bonding character. The EFG are determined at equilibrium with the TZVP basis set, except Sn and I centres where the basis set is TZV + MP2. For the bromo and iodo compounds, especially the latter, it is essential to allow for core polarisation, by decontraction of the p,d-functions. This is conveniently done by initial optimization of the structure with a partly contracted basis, followed by reestablishment of the equilibrium structure with the decontracted basis. A close correlation of the observed (microwave spectral) data with the calculations was observed, using the 'best' values for the atomic quadrupole moments for Cl, Br, and I; thus there seems no need to postulate that the value of Q_{Br} for ^{79}Br and ^{81}Br are in error. The SCF and MP2 wave-functions were converted into localised molecular orbitals by the Boys Method. This allowed a study of the differing s/p/d-hybridisation ratios, and the centroid positions, to be compared with the quadrupole coupling constants. The charge distributions for the atoms were converted into local bond dipoles, which in turn are correlated with the electronegativity differences of the bonded atoms.

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