Halogen Nuclear Quadrupole Coupling Constants in Non-axially symmetric Molecules; *Ab initio* Calculations, which Include Correlation, Compared 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 C_{2v}, C_{3v} and other symmetry molecules of general formula MH_2X_2 and MHX_3, where the halogen atoms (X) are Cl, Br and I, and the heavy central atoms (M) are C and Si. The study presents results at a standardised level of calculation, triple-zeta in the valence space plus polarisation functions (TZVP) for the equilibrium geometry stage; all-electron MP2 correlation is included in all these studies. For the bromo and iodo compounds, especially the latter, it is essential to allow 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.

The NQCCs, derived from the EFGs, using the 'best' values for the atomic quadruple moments Cl, Br and I, lead to good agreement with the inertial axis (IA) data obtained from microwave spectroscopy. When the data from the present study is plotted against the values derived from the IA data, obtained by whatever approximations chosen by the MW authors, we obtain a linear regression for the data (85 points) with the slope 1.0365 and intercept –0.1737, with standard errors of 0.0042 and 0.2042, respectively; these are statistically identical results irrespective of whether the data is restricted to IA or EFG principal axis (PA) data.

Since as in the C_{3v} MH_3X compounds studied previously, a close correlation of the microwave spectral data with the calculations was observed using the 'best' current values for Q_Z, there seems no need to postulate that the values of Q_{Br} for both ^{79}Br and ^{81}Br are seriously in error. A scaling downwards of Q_Z by about 5% for Br and I increases the agreement with experiment, but the contributions of relativistic effects are unknown, and could lead to further reassessment.

Of the two common assumptions used in MW spectroscopy, to convert from IA to EFG-PA data, either (a) cylindrical symmetry of the NQCC along the bond direction, or (b) coincidence of the tensor principal element with the bond axis, the latter is found to be a much more realistic approximation.

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