

PROBING WEAK BONDING INTERACTIONS THROUGH QUADROPOLAR COUPLING OF CHLORINE

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Among the most challenging aspects of spectral assignment in rotational spectroscopy are complex hyperfine coupling patterns and a flat potential energy surface with many stable conformers. Electronic structure calculations are an essential tool for predicting geometries and spectroscopic constants such as nuclear quadrupole splitting. Reliable predictions are therefore essential for a fast assignment process.

Computational data for 22 weakly bound chlorine containing complexes is compared to experimental spectroscopic data from literature. The chosen methods are commonly used among rotational spectroscopists for initial theoretical screening of a target system. Ab initio methods with a large basis set are found to perform best overall in prediction both the geometry of the complex and the quadrupolar coupling with moderate computational costs. As inexpensive calculations determining equilibrium structures disregard large amplitude motions, which are often observed in weakly-bound complexes. Inaccurate geometries result in an incorrect projection of the nuclear quadrupole coupling tensor into the principle axis system. The quality of nuclear quadrupole predictions overall decreases compared to monomer studies from William Bailey's quadrupolar coupling data set,^a which was focused on monomers. This study aims to expand upon Bailey's benchmarking dataset and cautions for critical evaluation of secondary parameters obtained from electronic structure calculations.

^aW. C. Bailey, Calculation of Nuclear Quadrupole Coupling Constants in Gaseous State Molecule, 2019, <https://nqcc.wcbailey.net/>