"Getting Highly Accurate Molecular Structures"

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Molecular structures determine spectroscopic parameters that allow molecular identification and reveal qualitative information about bonding and energetics. Over the years, a number of distinct operational definitions of molecular structure (bond lengths and bond angles) have emerged and some confusion often exists when theoreticians and experimentalists debate "a bond length". Here I briefly review the practical value of accurate molecular structures and survey existing experimental and theoretical methods for determining them. I place particular emphasis on the Kraitchman r_s substitution structure, the computationally derived r_e structure and the semi-experimental r_{se} structure. Ultimately, the most satisfactory method for determining very high-accuracy structures today is a mixed experimental-theoretical approach that uses data from microwave spectroscopy and quantum-chemical calculations. After discussing this and providing a few illustrative examples I present some recent results that target questions such as, "how accurately can one calculate molecular structures by brute force quantum chemistry?" and "how closely do these structures agree with the semi-experimental kind?"