

UNCERTAINTIES OF MOLECULAR STRUCTURAL PARAMETERS

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The most fundamental property of a molecule is its three-dimensional (3D) structure formed by its constituent atoms (see, *e.g.*, the perfectly regular hexagon associated with benzene). It is generally accepted that knowledge of the detailed structure of a molecule is a prerequisite to determine most of its other properties.

What nowadays is a seemingly simple concept, namely that molecules have a structure, was introduced into chemistry in the 19th century. Naturally, the word changed its meaning over the years. Elemental analysis, simple structural formulae, two-dimensional and then 3D structures mark the development of the concept to its modern meaning. When quantum physics and quantum chemistry emerged in the 1920s, the simple concept associating structure with a three-dimensional object seemingly gained a firm support. Nevertheless, what seems self-explanatory today is in fact not so straightforward to justify within quantum mechanics. In quantum chemistry the concept of an equilibrium structure of a molecule is tied to the Born–Oppenheimer approximation but beyond the adiabatic separation of the motions of the nuclei and the electrons the meaning of a structure is still slightly obscured.¹

Putting the conceptual difficulties aside, there are several experimental, empirical, and theoretical techniques to determine structures of molecules. One particular problem, strongly related to the question of uncertainties of “measured” or “computed” structural parameters, is that all the different techniques correspond to different structure definitions and thus yield different structural parameters. Experiments probing the structure of molecules rely on a number of structure definitions, to name just a few: r_0 , r_g , r_a , r_s , r_m , etc., and one should also consider the temperature dependence of most of these structural parameters which differ from each other in the way the rovibrational motions of the molecules are treated and how the averaging is performed. Simply, there are significant disagreements between the same bond length measured by different techniques. These disagreements are, however, systematic and can be computed via techniques of quantum chemistry which deal not only with the motions of the electrons (electronic structure theory) but also with the often large amplitude motions of the nuclei.

As to the relevant quantum chemical computations, since about 1970 electronic structure theory has become able to make quantitative predictions and thus challenge (or even overrule) many experiments. Nevertheless, quantitative agreement of quantum chemical results with experiment can only be expected when the motions of the atoms are also considered. In the fourth age of quantum chemistry² we are living in an era where one can bridge quantitatively the

gap between ‘effective’, experimental and ‘equilibrium’, computed structures at even elevated temperatures of interest thus minimizing any real uncertainties of structural parameters.³

The connections mentioned are extremely important as they help to understand the true uncertainty of measured structural parameters. Traditionally it is microwave (MW) and millimeterwave (MMW) spectroscopy, as well as gas-phase electron diffraction (GED), which yielded the most accurate structural parameters of molecules. The accuracy of the MW and GED experiments approached about 0.001 Å and 0.1° under ideal circumstances, worse, sometimes considerably worse, in less than ideal and much more often encountered situations.

Quantum chemistry can define both highly accurate equilibrium (so-called Born-Oppenheimer, r_e^{BO} , and semiexperimental, r_e^{SE}) structures and, via detailed investigation of molecular motions, accurate temperature-dependent rovibrationally averaged structures. Determining structures is still a rich field for research,⁴ understanding the measured or computed uncertainties of structures and structural parameters is still a challenge but there are firm and well-established guidelines. At present it seems that the best structures, both the most accurate ones and the ones easiest to compare when structural trends are sought, are the semiexperimental equilibrium structures. The r_e^{SE} structures are based on semiexperimental equilibrium rotational constants, B_e^{SE} , which are the corrected effective rotational constants B_0 “measured” for a given isotopologue and are corrected for the rovibrational effect using a computed cubic force field. The r_e^{SE} structure of the molecule is determined via a least-squares fit of the structural parameters to the B_e^{SE} s. During the large number of such structural studies, some on molecules as large and complex as amino acids, including glycine,⁵ alanine,⁶ and proline,⁷ it became clear that the “measured” rotational constants are often not accurate enough for the purposes of accurate structure determination and they need to be refitted using the method of predicate observations.^{4,8} The method of predicate observations can also be used during the structural fitting and yields more reliable and tighter uncertainties for the refined structural parameters. With the joint clever use of experiment and theory one can routinely achieve the 0.001 Å and 0.1° accuracy which previously could characterize only the most elaborate experiments.

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