ACCURATE EQUIBRIUM STRUCTURES: THEORY AND EXPERIMENT NEED EACH OTHER

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It is exceedingly difficult to determine molecular equilibrium structures to an accuracy of 0.001Å for bond lengths and *ca.* 0.2^o for angles. It is sometimes possible, in principle, to use microwave and rotationally resolved vibrational spectra to extract ground state rotational constants and the full set of vibration-rotation interaction constants. However, nature rarely cooperates and allows all of these parameters to be determined. Moreover, problems with Coriolis resonances often plague the rotationally analysis of excited vibrational levels in polyatomic molecules. Of course, electronic structure theory allows equilibrium structures to be determined directly. However, the levels of electron correlation treatment and the extraordinarily large basis sets required to achieve this level of accuracy are such that it quickly becomes intractable for all but the smallest species. In this talk, a combined approach will be summarized in which the ground state rotational constants obtained from microwave spectroscopy are combined with rotation-vibration constants from the anharmonic force field obtained from quantum chemical calculations. The effective equilibrium rotational constants obtained by this procedure are entirely free of problems associated with Coriolis resonance (which seems not well-known) and can be used to obtain the corresponding structures by least-squares refinement against isotopic data. Several examples will be given.