Ph.D. DISSERTATION DEFENSE

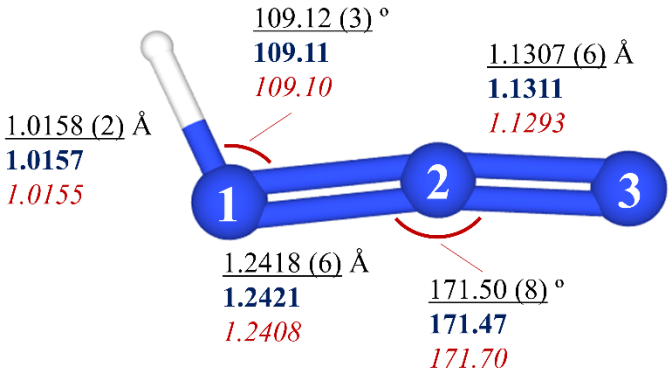
Andrew Owen

Computational Methods Applied to the Study of the Structure, Spectra, and Reactivity of Small Organic Molecules

McMahon | Woods Research Group

Friday, August 12th at 2:00 pm, Room 9341

The semi-experimental equilbrium structure (r_e^{SE}) for a molecule can be obtained through analysis of the rotational spectra of a molecule and of a sufficient number of isotopic substitutions, combined with theoretical calculations to account for effects of vibration and the distribution of electron mass. Our group has applied such analyses to several molecules and, owing to the high quality fitting of extensive amounts of rotational spectra, can determine the r_e^{SE} structure of a molecule to high precision. The precision is such that a single *ab initio* structure optimization is insufficient to replicate the structure to within the statistical uncertainty of the fitting procedure used to obtain the r_e^{SE} structure: for hydrazoic acid (HN_3), only two structural parameters from a CCSD(T)/cc-pCV6Z optimization agreed with the r_e^{SE} values. It is thus necessary to apply corrections to account for electron correlation and the effects of relativity and of the Born-Oppenheimer approximation, resulting in a "best theoretical estimate" (BTE). The equilibrium structure of HN_3 resulting from application of the r_e^{SE} and BTE methodologies is presented, and the dependence of these methodologies on the size of the basis set is discussed, along with an analysis that strongly supports that the r_e^{SE} structure is not only highly precise, but also highly accurate. Finally, noting that the fitting of rotational spectra can be complicated by the presence of vibration-rotation coupling, preliminary efforts towards obtaining theoretical predictions of vibration-rotation coupling constants are discussed.



Equilibrium Structures Of Hydrazoic Acid (HN_3)

Semi-Experimental (r_e^{SE})
Best Theoretical Estimate (r_e)
CCSD(T)/cc-pCV6Z (r_e)

Department of Chemistry
UNIVERSITY OF WISCONSIN-MADISON