**Comparison of the quality of DFT versus MP2 and MP3 total energies and an unexpected size effect in the conformational equilibria of vinylhalogermanes.** Forner, Wolfgang; Badawi, Hassan M.; Seddigi, Zaki S. Department of Chemistry, King Fahd University of Petroleum & Minerals, Dhahran, Saudi Arabia. Asian Journal of Spectroscopy (2006), 10(1&2), 15-35.

## Abstract

CH2:CHGeClH2, CH2:CHGeCl2H and fluoro analogs were studied by DFT-B3LYP/6-311++G** and ab initio MP2/ 6-311++G** calcns. The potential functions for the internal rotation of the GeClH2, GeCl2H and fluoro-analog rotors were calcd. and they are very similar for the mols. In both halogen derivs., both mols. exhibit a conformational equil. between the two stable cis and gauche forms, where in all cases the trans conformation is one of the two transition states. In the case of the vinylmonohalogermanes the gauche forms are slightly lower than the cis ones, while in the case of vinyldihalogermanes the two forms are nearly degenerate. The equil. consts. of the four equil. were calcd. and are presented. The vibrational frequencies of the two mols. in their stable conformations were computed. The potential energy distributions, PED, among the symmetry coordinates of the normal modes of the vinylchlorogermanes were calcd. from normal coordinate calcns. and a complete assignment of all spectral modes is provided. Further the IR and vibrational Raman spectra of the conformational equil. were plotted and shown. Due to previous experience with comparisons between calcd. and exptl. spectra, the authors expect them to be rather reliable predictions of the corresponding exptl. ones, esp. because instead of relative energies the authors use now equil. consts. calcd. from Gibbs free energies to det. the populations of the mols. in the equil. It is pointed out, that in previous findings in systems with lower electron densities (C instead of Ge) usually MP2 yields better total, and thus also better relative energies than DFT. Since for higher electron densities, MP2 which includes only double excitations could deteriorate in comparison to DFT because of the higher importance of triple and quadruple excitations, the authors decided to study halogermanes of increasing electron densities to study this possibility.

Indeed, in the present cases DFT total energies seem to be of similar reliability as MP2 ones in case of the fluoro derivs. and much better than MP2 ones for the chloro derivs., the latter having the higher electron densities. Thus it seems that besides the principle theor. deficiency of size inconsistency from which all truncated CI expansions suffer, but not MP in any order, there appears to be another size problem: with increasing electron d. the probability and thus importance of higher order excitations (MP2 includes only doubles and these not completely) increases. It seems, as shown here on the example of vinylhalogermanes, that such effects are implicitly included in the B3LYP functional of DFT. The authors' MP3 calcns. on the chlorogermanes showed, that the effects are small, because MP3 still includes only double excitations, but they are shifting the MP results slightly towards the DFT ones.