

Comparison of the conformational stability for several vinylhalomethanes and silanes with experiment using MP2 perturbation theory and DFT. Forner, Wolfgang; Badawi, Hassan M.. Department of Chemistry, King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia. Collection of Czechoslovak Chemical Communications (2007), 72(1), 15-50.

Abstract

In recent literature it was reported that the valence triple zeta basis set augmented by polarization functions is not too reliable for vinyl monohalo- and dihalomethanes and -silanes, the halogen being fluorine and chlorine. The major conclusion was that a valence triple zeta basis is too small to be augmented by polarization functions in a balanced way, at least on vinylmonofluoromethane. Thus we decided to apply the 6-311++G** basis set to the complete series of methanes, silanes and germanes (the latter ones are just added for completeness because no exptl. data are available for them and, moreover, we published them already previously) and to compare the results to exptl. data available in the literature to see whether the failures of this basis set show up in the complete series of mols. In the literature we found five such mols. and the information which of the conformers is the most stable. Indeed we found that predictions on the relative stability of conformers in those systems with this basis set and MP2 as well as DFT are with a 60:40 chance, three being correct predictions and two being incorrect ones out of the five. However, since the energy differences are rather small in these systems and due to the fact that - as a consequence of twofold degeneracy of the gauche conformer on the potential curve of the torsional vibration - the abundances of the conformers in equil. do not change too much, we decided to calc. also vibrational spectra for three examples and to compare them also to expt. It is reported that besides the failures in total energy (we have chosen two examples where predictions of the nature of the stable conformer are correct, and one where it is not), the vibrational spectra are rather well reproduced, esp. when exptl. energies are used to calc. abundances in equil. in the case where the prediction of the stable conformer failed.