

Theoretical vibrational spectra of cyclohexanecarboxaldehyde. Foerner, Wolfgang; Badawi, Hassan M.. Dep. Chem., King Fahd Univ. Petroleum Minerals, Dhahran, Saudi Arabia. *Journal of Molecular Modeling* [online computer file] (2001), 7(8), 288-305.

Abstract

Vibrational spectra of cyclohexanecarboxaldehyde are calcd. with d. functional theory using the B3LYP functional together with a 6-311++G** basis set are presented. The results in the case of the IR spectrum of the mixt. of conformers at 300 K are compared with the exptl. spectrum and, apart from the intensities of the CH and CO stretches, reasonable agreement is found. These deficiencies can be traced back to the well-known nonlinearities in case of CH stretches and the CO stretch. Potential energy distributions among symmetry coordinates in each normal mode are presented and used to assign specific at. movements to each of the modes. Potential energy scans for the CHO rotor in both the axial and equatorial conformers are presented and barrier heights are compared with previous Hartree-Fock calcns. and exptl. data. It is reported that there could be three stable conformers, namely equatorial-gauche (eg), which is the most stable, equatorial-trans (et) and axial-gauche (ag). The optimized energies of all the min. and of the transition states are presented. However, comparison of the calcd. spectrum with the exptl. one indicates that total energies are slightly in error and that in the mixt. of conformers no ag is present and thus the et to eg ratio is also different. Using exptl. values for relative energies of conformers, we could obtain spectra in fair agreement with expt. This indicates that when only total energy differences are calcd., slight errors in them play a role because of the very small relative energies in this case, while properties like geometries and spectra, which depend not on energy differences but on anal. calcd. energy derivs., are not affected.