THE STRUCTURE, SPECTRA AND PUCKERING BARRIER OF CYCLOBUTANE: A THEORETICAL STUDY

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We present the results of high level $ab\ initio$ calculations for the structure, harmonic and anharmonic spectroscopic constants and puckering barrier of cyclobutane in an effort to establish the minimum theoretical requirements needed for their accurate description. We found that accurate estimates for the barrier between the minimum (D_{2d}) and transition state (D_{4h}) configurations require both higher levels of electron correlation [MP4, CCSD(T)] and basis sets of quadruple-ζ quality or larger. By performing CCSD(T) calculations with basis sets as large as cc-pV5Z we were able to obtain, for the first time, a calculated value of 498 cm^{-1} for the puckering barrier that lies within 18 cm^{-1} (or 4%) of the experimental value [a] whereas the best previously calculated values [b] had errors exceeding 40% of experiment. Our best computed values (at the CCSD(T)/aug-cc-pVTZ level of theory) for the equilibrium structural parameters of C_4H_8 are R(C$-$C) $= 1.554$ $\AA$, R(C$-$H$_\alpha$) $= 1.093$ $\AA$, R(C$-$H$_\beta$) $= 1.091$ $\AA$, ϕ(C$-$C$-$C) $= 88.1^\circ$, α(H$_\alpha$$-C-H_\beta$) $= 109.15^\circ$ and $\theta = 29.68^\circ$ for the puckering angle. We furthermore present anharmonic calculations that are based on a second-order perturbative evaluation of rovibrational parameters and their effects on the vibrational spectra and average structure. We have found that the anharmonic calculations predict the experimentally measured fundamental band origins within 1% (30 cm^{-1}) for most vibrations. The results of the current study can serve as a guide for future calculations on the substituted four-member ring hydrocarbon compounds.

[a] T.B. Malloy and W.J. Lafferty, J. Molec. Spectrosc. 54 20 (1975).
[b] D. Henseler and G. Hohlneicher, J. Phys. Chem. A 102 10828 (1998).