

VIBRATIONAL ANHARMONICITY IN ETHYLENE, METHYL FLUORIDE AND DICHLOROMETHANE: AN EXPLORATION USING GAUSSIAN 03

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This survey was undertaken (a) to test the suitability of the program Gaussian 03 (G03) for anharmonicity calculations: (b) to compare results for different models (B3LYP, MP2) and basis sets (6-311++G\*\*, cc-pVTZ): (c) to see if anharmonicity corrections to harmonic frequencies were identical for different types of C-H stretching vibration. Results to be presented show that the version of G03 available was inadequate to detect familiar instances of Fermi resonance. For  $C_{3v}$ -type molecules G03 yielded anharmonicity constants  $x_{i,j}$  unusable by the experimentalist. In  $\text{CH}_2\text{Cl}_2$  the antisymmetric C-H stretching frequency is associated with a larger anharmonicity correction than is the case for the C-H stretch, in a situation where Fermi resonance is negligible. Calculated values of  $x_{1,1}$ ,  $x_{1,6}$  and  $x_{6,6}$  for  $\text{CH}_2\text{Cl}_2$  agree excellently with experimental data. In ethylene a marked effect of basis set was found in MP2 calculations for the out-of-plane bending modes, linked to the presence or absence of  $f$  functions.