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 CH_2Cl_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 CH_2Cl_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.