ON IMPLEMENTATION OF A SMALL-AMPLITUDE VIBRATIONAL FORMALISM IN MOLECULES WITH LARGE-AMPLITUDE INTERNAL ROTATION: TORSIONAL ANGLE DEFINITION AND PROJECTED VIBRATIONAL FREQUENCIES

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This talk will concern itself primarily with three questions: (i) What is the range of commonly used definitions for the internal rotation angle, and how do variations within this range affect intercomparisons among Hamiltonians and fitting results from various laboratories? (ii) Do variations with internal rotation angle of the projected force constants delivered by present commercial quantum chemistry packages have sufficient precision to allow meaningful extraction of $ab\ initio$ higher order torsion-rotation interaction terms? (iii) What fraction of the extensive chemical reaction dynamics literature can be easily adapted for use in high-resolution spectroscopic studies of small-amplitude vibrations in methyl top internal rotor molecules? Answers to these questions will be discussed both from an algebraic and from a numerical computation point of view.