THE OVERTONE SPECTRUM AND POTENTIAL ENERGY SURFACE OF METHYL FLUORIDE

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Variational methods are presented for calculating excited stretching and (separately) bending vibrational states of C_{3v} symmetry centrally connected penta-atomic molecules. The use of Radau vectors to describe the internal coordinates greatly simplifies the derivation, form and application of the exact kinetic energy operator and symmetry is used to reduce the size of the secular matrices to be diagonalised. The code does not assume any particular functional form for the potential energy surface (PES). Difficulties associated with redundancy in the angular internal coordinates are discussed.

A four dimensional stretching PES for methyl fluoride has been determined by fitting to 2000 (symmetrically unique) *ab initio* points calculated at the CCSD(T) level. A five dimensional bending PES has been determined based on a further 1500 points. Pure stretching and pure bending excited vibrational state variational calculations for CH_3F are presented. These states will be used to represent the stretching and bending motions in fully coupled stretch-bend calculations which will ultimately resolve problems of assignment and interpretation of the infrared and near infrared overtone spectra of CH_3F.