DIABATIC VERSUS ADIABATIC CALCULATION OF TORSION-VIBRATION INTERACTIONS

JON T. HOUGEN, *Sensor Science Division, NIST, Gaithersburg, MD 20899-8441, USA*.

The introductory part of this talk will deal briefly with two historical topics: (i) use of the words adiabatic, nonadiabatic, and diabatic in thermodynamics and quantum mechanics, and (ii) application of diabatic and adiabatic ideas to vibrational energy level calculations for a pair of diatomic-molecule potential energy curves exhibiting an avoided crossing. The main part of the talk will be devoted to recent work with Li-Hong Xu and Ron Lees on how ab initio projected frequency calculations for small-amplitude vibrations along the large-amplitude internal rotation path in methanol can best be used to help guide experimental assignments and fits in the IR vibrational spectrum. The three CH stretching vibrations for CH_3OH can conveniently be represented as coefficients multiplying three different types of basis vibrations, i.e., as coefficients of: (i) the local mode C-H_i bond displacements δr_i for hydrogens H_1, H_2 and H_3 of the methyl top, (ii) symmetrized linear combinations of the three δr_i of species $A_1 \oplus E$ in the permutation-inversion group $G_6 = C_{3v}$ appropriate for methanol, or (iii) symmetrized linear combinations of the three δr_i of species $2A_1 \oplus A_2$ in the permutation-inversion group G_6. In this talk, we will focus on diabatic and adiabatic computations for the $A_1 \oplus E$ basis vibrations of case (ii) above. We will briefly explain how Jahn-Teller-like and Renner-Teller-like torsion-vibration interaction terms occurring in the potential energy expression in the diabatic calculation become torsion-vibration Coriolis interaction terms occurring in the kinetic energy expression of the adiabatic calculations, and also show how, for algebraically solvable parameter choices, the same energy levels are obtained from either calculation. A final conclusion as to which approach is computationally superior for the numerical data given in a quantum chemistry output file has not yet been arrived at.