

## THEORETICAL QUESTIONS ASSOCIATED WITH UTILIZING AB INITIO RESULTS TO AID IN INTERPRETATION OF VIBRATION-TORSION-ROTATION SPECTRA

JON T. HOUGEN, MIRZA A. MEKHTIEV, *Optical Technology Division, National Institute of Standards and Technology, Gaithersburg, MD USA 20899-8441*; LI-HONG XU, *Department of Physical Sciences, University of New Brunswick, Saint John, N.B., Canada E2L 4L5*; RONALD M. LEES, *Department of Physics, University of New Brunswick, Fredericton, N.B., Canada E3B 5A3*.

This talk will discuss several questions which arise when trying to connect *ab initio* results with molecular parameters in phenomenological torsion-rotation and vibration-torsion-rotation fitting Hamiltonians, and for which we now have varying degrees of understanding: (1) How are the various definitions of the torsional angle (intrinsic reaction coordinate, average of three dihedral angles,  $\gamma$ 's in torsional Hamiltonians in the literature, etc.) related? Short answer: they differ by a Fourier series in  $\sin 3n\gamma$ . (2) How can we determine the rho axis system in a flexible internal rotor molecule? Short answer: use an instantaneous rho system determined from the moment of inertia and the angular momentum generated at each point along the internal rotation path. (3) How exactly are partial derivatives (of atom positions, moment of inertia tensor, etc.) with respect to  $3N - 6$  internal coordinates to be related to partial derivatives with respect to one large amplitude coordinate and  $3N - 7$  small amplitude vibrational coordinates at various points along the internal rotation path? How exactly are the  $(3N - 6) \times (3N - 6)$   $\mathbf{F}$  (force constant),  $\mathbf{G}$  (reduced mass), and  $\mathbf{GF}$  matrices to be converted to  $(3N - 7) \times (3N - 7)$  quantities when the torsional degree of freedom is removed from the small-amplitude vibrational problem? Short answer: project out the torsional angle direction in the  $3N - 6$  space and throw it away. (4) How are the  $C_{3v}$  permutation-inversion symmetry species  $A_1, A_2, E$  to be used in the vibrational problem after motion along the internal rotational path causes the  $C_s$  point group symmetry species  $A', A''$  to be lost? Short answer: work in progress. (5) How does setting certain terms to zero in the fitting Hamiltonian, which in turn implies certain reduction schemes, change the values of other phenomenological Hamiltonian parameters of lower, the same, or higher order, so that they are no longer directly comparable with *ab initio* output? Short answer: work in progress. Concrete illustrations of numerical answers to some of these questions for the methanol molecule will be given in the following talk.