TORSIONAL AND K-ROTATIONAL LABELING PROBLEMS FOR EIGENVECTORS FROM LARGE INTERNAL ROTOR CALCULATIONS INVOLVING ONE METHYL TOP

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The problem of attaching torsional and rotational quantum number labels to computer-generated numerical eigenvectors with extensive basis set mixing is considered for the internal-rotation−overall-rotation problem in molecules with one methyl top. Quantum number labeling problems arise physically because the torsion and the K-rotation degrees of freedom both pass from one limiting case to another as the torsional energy moves from below the top of the internal rotation barrier to above it, i.e., the torsional degree of freedom changes from a vibration to an internal rotation, while the K-rotational degree of freedom moves its direction of quantization from a principal axis to an axis depending also on angular momentum generated by the methyl top rotation. Since the choice of axis system, basis set, and computational scheme all influence the eigenfunction labeling procedure, consideration is limited here to a commonly used two-step matrix-diagonalization scheme. Torsional labels for eigenfunctions generated in the first diagonalization step are chosen by maximizing certain ΔK = 1 overlap integrals (described in the preceding talk). K-rotational labels are chosen after the second diagonalization step according to angular momentum projections along axes passing through stationary points of appropriate rotational energy surfaces. Results will be described for rotational energy levels of CH_3CHO in torsional states below and above the barrier, with rotational quantum numbers in the range $J \leq 20$ and $K_{\mathrm{a}} \leq 15$.