A NEW SCHEME OF K-LABELING FOR TORSION-ROTATION ENERGY LEVELS IN LOW-BARRIER MOLECULES

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The problem of attaching K rotational quantum number labels after the second diagonalization step in the rho-axis-method treatment of methyl-top internal rotation problems is considered. A new partially computer-automated labeling scheme for K-labeling is proposed. The scheme is rather simple and does not require any information other than that provided by the numerical eigenvectors obtained after diagonalization of the torsion-rotation Hamiltonian matrix. It assumes that within a given K stack, torsion-rotation eigenfunctions vary slowly when J changes by unity. The basic idea is thus to search for similarities in basis-set composition in torsion-rotation eigenvectors belonging to adjacent J values. In such a way, torsion-rotation states of adjacent J values having the same value of K are connected. This allows one to transfer a given K label from lower J values, where it can be determined easily (either from eigenvector composition or from energy ordering considerations), to higher J values, which are characterized by extensive basis set mixing. The approach was successfully applied to the K-labeling problem of prolate (acetaldehyde, methanol, ethyl acetamidoacetate) and oblate (acetic acid, acetamide) rotors characterized by significant torsion-rotation interactions in their spectra. The scheme gives correct K-labels for eigenvectors in the majority of cases. The problems with the remaining cases are mainly caused by localized avoided crossing interactions, which can be fixed relatively easily in manual mode using a graphical visualization of the torsion-rotation energy level diagram.