EXTENDED PERMUTATION-INVERSION GROUPS FOR SIMULTANEOUS TREATMENT OF THE ROVIBRONIC STATES OF TRANS-ACETYLENE, CIS-ACETYLENE, AND VINYLIDENE

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The electronic ground state potential surface of acetylene (HCCH) has a minimum at the linear conformation, but the excited electronic states may have potential minima at a variety of nonlinear equilibrium shapes. This work is concerned with the group theoretical ideas necessary to treat simultaneously the symmetry properties of rovibronic states associated with three different planar acetylene equilibrium configurations, namely trans bent acetylene, cis bent acetylene, and vinylidene (H2C=C). We make use of three different kinds of groups: (i) point groups, (ii) permutation-inversion (PI) groups, and (iii) extended PI groups. The PI group is G_4 or G_8, depending on whether C-H bond breaking is impossible (no bent acetylene $\leftrightarrow$ vinylidene interconversion), or possible. The extended PI groups are $G_4^{(2)}$ and $G_8^{(2)}$, respectively, when the only large amplitude motions are the CCH bends at each end of the molecule, and $G_4^{(8)}$ and $G_8^{(8)}$, respectively, when internal rotation is added as a third large amplitude motion. Applied to acetylene, the results indicate that there will be no splittings of the rovibronic levels unless CH bond breaking occurs. Even without bond breaking, however, states of the cis and trans isomers just below their interconversion barrier will show staggerings in their K-structures, i.e., a given vibrational level will have three tunneling components at slightly different energies: one component will have levels with $K = 4n$ only (where n is an integer), a second component will have levels with $K = 4n+2$ only, and the third will have only odd-K levels. New experimental results for the S_1-cis electronic state of acetylene are reviewed, and are found to be consistent with the group theory in so far as comparison is possible.