ABNORMAL REVERSED SPLITTINGS OF TORSIONAL SUBLEVELS INDUCED BY INVERSION MOTION IN THE S_1 STATE OF ACETALDEHYDE

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The G_6 group-theoretical high-barrier formalism developed previously for internally rotating and inverting CH_3NHD is used to interpret the abnormal torsional splittings in the S_1 state of acetaldehyde for levels $14^{0-}15^0$, $14^{0-}15^1$ and$14^{0-}15^2$, in which 14^{0-} denotes the asymmetric inversion tunneling component of the aldehyde hydrogen and 15 denotes vibrational mode for the methyl torsional motion. This formalism, derived using an extended permutation-inversion group $G_6{}^m$, treats simultaneously methyl torsion tunneling, aldehyde hydrogen inversion tunneling and overall rotation. Fits to the rotational states of the four pairs of inversion-torsion vibrational levels ($14^{0+}15^0$, $14^{0-}15^0$), ($14^{0+}15^1$, $14^{0-}15^1$), ($14^{0+}15^2$, $14^{0-}15^2$), and ($14^{0+}15^3$, $14^{0-}15^3$) are performed, giving rms deviations of 0.003, 0.003, 0.004 and 0.004 cm^{-1}, respectively, in which the deviations are comparable with the experimental uncertainty 0.003 cm^{-1}. For torsional levels lying near the summit of the torsional barrier, this theoretical model including high-order terms provides satisfactory fits to the experimental data. The K structures deviated from a pure torsional rotor are fitted using this formalism and are proved to be from coupling to aldehyde hydrogen inversion.