TORSIONAL SPLITTINGS IN SMALL-AMPLITUDE VIBRATIONAL FUNDAMENTAL STATES OF METHANOL-TYPE MOLECULES

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Group-theoretical methods are used to show that inverted torsional splittings in fundamental levels of small-amplitude vibrations of methanol-like molecules can be parametrized and understood in terms of the energy level patterns induced when a pair of high-barrier torsionally split components of given \( \nu \) and \( ^1A + ^1E \) symmetry species in the molecular symmetry group \( G_6 \) is allowed to interact with small-amplitude vibrational modes of symmetry \( \nu E \). Such doubly degenerate \( \nu E \) vibrational modes arise rather naturally in \( G_6 \) (isomorphic with the point-group \( C_{3v} \)) for those methyl-group vibrations in point-group-\( C_\alpha \) asymmetric tops like \( \text{CH}_3\text{CHO} \) that are analogs of the degenerate methyl-group stretch, bend, and rocking vibrations in point-group-\( C_{3v} \) symmetric tops like \( \text{CH}_3\text{C}≡\text{C-H} \). The present group-theoretical treatment is somewhat different than, but (as a comparison of model parameters shows) still fundamentally similar to, the recent local mode explanation of inverted torsional splittings in the C-H stretching fundamental region in methanol. The formalism has been applied to new torsional splitting data for the \( \text{CH}_3 \)-rocking modes, and is found to give moderate agreement.