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

JON T. HOUGEN, *Optical Technology Division, National Institute of Standards and Technology, Gaithersburg, MD 20899-8441*; RONALD M. LEES, *Department of Physical Sciences, University of New Brunswick, Saint John, NB E2L 4L5, Canada*.

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 v_t and ^{t}A + ^{t}E symmetry species in the molecular symmetry group G_6 is allowed to interact with small-amplitude vibrational modes of symmetry ^{v}E. Such doubly degenerate ^{v}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_s asymmetric tops like CH_3-CHO that are analogs of the degenerate methyl-group stretch, bend, and rocking vibrations in point-group-C_{3v} symmetric tops like CH_3-C≡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 CH_3-rocking modes, and is found to give moderate agreement.