TORSION-INVERSION TUNNELING PATTERNS IN THE CH-STRETCH VIBRATIONALLY EXCITED STATES OF THE G_{12} MOLECULES

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Torsion-inversion tunneling models have been developed for CH-stretch vibrationally excited states in G_{12} molecules, including 2-methylmalonaldehyde (2-MMA), 5-methyltropolone (5-MT), and methylamine. These models are extensions of the group theoretical approach of Hougen[a] and the internal coordinate model of Wang and Perry[b] in which the inversion motion is included in addition to the torsion and the small-amplitude (e.g., CH stretch) vibrations. The present models incorporate torsion-inversion tunneling parameters h_{2V} and h_{3V}, respectively and a number of low-order terms couplings to the CH-stretch vibrations. Of the three methyl CH stretch vibrations, Model I includes only the two asymmetric stretches that correlate to the E-type degenerate CH stretch in a symmetric rotor; Model II includes all three. The models yield the torsion-inversion tunneling patterns of the four symmetry species, A, B, E_1 and E_2, in the CH-stretch excited states. The principal results are as follows. (i) Both models and each of the coupling terms considered yield the same tunneling patterns, which are different in the asymmetric CH stretch excited states as compared to those in the ground state. (ii) In Model I, the magnitude of the tunneling splittings in the two asymmetric CH stretch excited states is exactly half of that in the ground state. (iii) In Model II, the relative magnitude of these splittings depends on the ratio $|\mu|/(|h_{2V}|+|h_{3V}|)$ where μ is the torsion-inversion-vibration coupling parameter. This ratio varies from 3 to 308 across the series methanol, methylamine, 2-methylmalonaldehyde and 5-methyltropolone, with a consequent variation in the magnitude of the tunneling splittings.

[a] J. T. Hougen *J. Mol. Spectrosc.* **207**, 60, (2001).
[b] X. Wang and D. S. Perry *J. Chem. Phys.* **109**, 10795, (1998).