TWO MODEL HAMILTONIANS FOR TORSION-INVERSION TUNNELING IN THE CH-STRETCH VIBRATIONALLY EXCITED STATES OF METHYLAMINE

MAHESH B DAWADI, AND DAVID S PERRY, *Department of Chemistry, The University of Akron, OH 44325-3601*.

In methylamine (CH_3NH_2), there are six equivalent mimina that are connected by torsion and inversion tunneling. In the G_{12} molecular symmetric group, there are four species, $A = \{A_1, A_2\}$, $B = \{B_1, B_2\}$, E_1 and E_2 that combine with distinct nuclear states. The ground vibrational state of CH_3NH_2 is split by torsion and inversion tunneling into a multiplet pattern of four distinct energy levels[a]. The experimental tunneling pattern for CH_3NH_2 in the ν_{11} asymmetric CH-stretch fundamental has been previously reported at this meeting. In the experimental pattern, the degenerate species (E_1 and E_2) are at the top and bottom of the multiplet and the non-degenerate species (B and A) are between them. In this work, we present two models for the torsion-inversion tunneling behavior in the CH-stretch excited states. Each model includes the lowest order torsion-inversion-vibration interactions available in the context of the model. The first model, which extends Hougen's treatment of methanol,[b] couples the two vibrational angular momentum components of the asymmetric CH-stretches to the large-amplitude motion to yield predicted tunneling patterns for the ν_2 and ν_{11} fundamentals. This model gives similar patterns for ν_2 and ν_{11}, in which E_1 and E_2 are in the middle of the multiplet and the non-degenerate species are at the top and bottom. The second model, which follows conceptually Wang and Perry's local mode treatment of methanol,[c] couples the three local CH-stretches to each other and to the large-amplitude motion to yield the tunneling patterns for the ν_2, ν_3 and ν_{11} fundamentals. For this model, we found that, for ν_2 and ν_{11}, both E_1 and E_2 are at the bottom of the multiplet, in contrast to ν_3 and the ground state where they are at the top. The fact that neither model reproduces the observed tunneling pattern for ν_{11}, suggests that additional isolated perturbations or systematic interactions are present in the experimental spectra.

[a] V.V. Ilyshin et al.*J. Mol. Spectrosc.* **251**(56-63), 2008.
[b] J.T. Hougen *J. Mol. Spectrosc.* **207**(60-65), 2001.
[c] X. Wang and D.S. Perry *J. Chem. Phys.* **109**(10795-10805), 1998.