Coupling of Large-Amplitude and Small Amplitude Vibrations in G_{12} Molecules

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Molecules with G_{12} symmetry, including methylamine, nitromethane, ethyl radical, protonated methanol, 2-methylmalonadlehyde (2-MMA) and 5-methyltropolone (5-MT) represent a class of molecules with six equivalent minimum energy geometries that are connected, in most of the molecules, by two large-amplitude degrees of freedom. One large-amplitude vibration is a 3-fold methyl internal rotor and the other has a 2-fold symmetric coordinate, which is either and an XY_2 wag (X = C, O, N, and Y = H, O) or a proton transfer.

Two simple models for the high-barrier tunneling behavior in the methyl CH stretch excited states are reported. These models are extensions of the group theoretical approach of Hougen [1] and the internal coordinate model of Wang and Perry [2]. The pattern of the four tunneling states (A, B, E_1 and E_2 symmetries) is predicted to be inverted in the asymmetric CH stretch excited states relative to the ground state. The trends in the patterns relative to tunneling rates and coupling parameters is presented and comparison is made to the available experimental data.

The couplings between the large-amplitude (LAV) and small-amplitude (SAV) vibrations stem from the variation of the SAV force constants in the 2-D space of the LAV's. First principles 2-D maps of the variation of the CH-stretch force constants LAV coordinates is reported. Although the torsional barriers differ by more than a factor of 20, the torsion-inversion-vibration coupling patterns are very similar for CH_3NH_2 and $CH_3CH_2^{\cdot}$. On the other hand, the torsion-inversion-vibration coupling in the charged species $CH_3OH_2^+$ is much weaker and qualitatively different in form.

High resolution experimental studies are underway to probe these phenomena. The ν_{11} asymmetric CH stretch band in CH_3NH_2 has a tunneling patterns heavily impacted by perturbations and hence different both from the ground state and from the theoretical predictions [3]. High-resolution spectra on CH_3NO_2 from Far-Infrared beamline at the Canadian Light Source (NO_2 wags, ν_7 and ν_8; NO sym bend, ν_4; CN stretch, ν_2) and from the Environmental Molecular Science Lab at the Pacific Northwest National Laboratory (NO asym stretch, ν_6) are in different stages of analysis and preparation for publication.

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