EXPERIMENTAL EVIDENCE OF LOCAL MODE BEHAVIOR IN MOLECULAR SPECTRA

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Low lying energy levels of molecules are usually well modeled using the normal mode picture. However when going higher and higher in energy this description is less and less valid, the vibrational quantum numbers loosing their physical meaning (in particular for hydrides). In fact at high energies for a number of molecules a local mode description is better suited. It is the purpose of this talk to show some experimental evidence of such a behavior.

As far as asymmetric top molecules are concerned, examples will be given both for highly excited vibrational states (H₂S molecule) and for high J and K_a quantum numbers (H₂Se, H₂Te molecules). In this latter case the rotational levels form four-member groups of nearly degenerate levels called energy clusters: Type 1 clusters for isolated vibrational states such as (000) or (010), type 2 clusters for interacting states such as {(100),(001),(020)}. Symmetric top molecules like H₃GeD reach local mode behavior already at moderate excitation (v = 2, 3...) of the Ge–H stretching motion. Characteristic features of such states are the dynamic symmetry lowering ($C_{2v} \rightarrow C_s$) with quenching of Coriolis effects, and the validity of simple relations between molecular parameters occurring in the conventional normal mode picture.