ROVIBRONIC ENERGY TOPOGRAPHY II: MOLECULAR INTERNAL-MOMENTUM EFFECTS AND MULIT-RES RESONANCE IN HIGH SYMMETRY MOLECULES

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Multi-surface rotational-energy-surfaces (RES) help to unravel Coriolis effects involving molecules with internal angular momentum due to nuclear spin, hindered rotors, or rovibronic coupling[a b]. Fine and superfine spectral structures may show markedly different sensitivity to relative strength of scalar ($B\zeta$) and tensor Coriolis coupling and to the total angular momentum quantum value J.
Unstable saddle points are often located on axes of C_2 local symmetry. RES plots show how they are stabilized by resonant Coriolis spin or vibronic interactions. This applies to molecules of symmetry ranging from asymmetric up to octahedral or icosahedral. Spectral signatures of this includes increased clustering and species mixing. An example involving v_3 fundamentals in XY_6 molecular models shows appearance of 12-fold rovibrational cluster degeneracy.
The resulting selective breakdown of Born-Oppenheimer-approximate (BOA) quantum numbers is analyzed by examining topography of multiple RES surfaces and by comparing their results to full-diagonalization eigensolutions.

[a] W.G. Harter, Computer Physics Reports **8**, 319 (1988).
[b] Ortigoso, Kleiner, Hougen: J. Chem. Phys. **110**, 11688 (1999).