Advanced models and the corresponding programs have been developed in the Dijon group to fit and model spectra of molecules possessing a high symmetry (tetrahedral or octahedral) at equilibrium like CH₄, SF₆, etc. These models, based on the use of group theory and tensorial developments have proved their high efficiency and can even be used for lower-symmetry species. Such developments, based on the expansion of effective Hamiltonian and transition operators, require, however, initial sets of molecular parameters in order to start the assignment of spectral lines. In some cases, this is not obvious at all, the detailed vibrational structure being largely unknown. The difficulty for molecules with high symmetry is that most excited vibrational levels split into several sublevels. Often, this splitting, and even the sublevel ordering, is not known. We will present some examples of such cases. This concerns small excited states of some small atmospheric molecules (SF₆, CF₄) implied into hot bands and also some larger carbon-cage molecules with many modes like cubane, adamantane, HMT.