# TENSORIAL DEVELOPMENT FOR THE ROVIBRONIC HAMILTONIAN AND TRANSITION MOMENTS OF OCTAHEDRAL $XY_6$ MOLECULES IN A FOURFOLD DEGENERATE ELECTRONIC STATE

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Some transition-metal hexafluorides like $ReF_6$, $OsF_6$ or $IrF_6$ have the particularity to posses a incomplete electronic subshell leading to low-lying degenerate electronic states. The ground electronic state is generally also degenerate. This implies the existence of very complex rovibronic couplings and thus the observation of unusual spectra[a,b]
A few years ago, we have elaborated a tensorial formalism adapted to octahedral molecules with an odd number of electrons[c] (*i.e.* with half-integer angular momenta), defining the $O_h^S$ group as the octahedron point group with its spinorial representations. We also presented a systematic tensorial development in the $SU(2) \otimes C_I \supset O_h^S$ group chain for the vibronic Hamiltonian of an octahedral molecule in a fourfold degenerate electronic state[d] of symmetry $G'_g$. However, this development had the disadvantage to lead to infinite matrices, due to the particular form of the vibronic coupling terms (Jahn-Teller, ...). Moreover, the molecular rotation was not included. In this talk, we present a systematic tensorial development of the full effective rovibronic Hamiltonian for a given vibronic polyad in a $G'_g$ electronic state. A construction of the form

$$\widetilde{H} = \sum_i \widetilde{t}_i \left( (E^{(\Gamma_e)} \otimes V^{(\Gamma_v)})^{(\Gamma)} \otimes R^{(\Gamma)} \right)^{(A_{1g})}$$

is proposed, where we define electronic operators $E^{(\Gamma_e)}$. This Hamiltonian has now finite matrices in the basis of the considered polyad. A similar construction is also given for the transition moment operators (dipole moment and polarizability) which are necessary to calculate transition intensities.

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[b] V. Boudon, M. Rotger and D. Avignant *J. Mol. Spectrosc.* **175**, 327–339 (1996).
[c] V. Boudon, and F. Michelot *J. Mol. Spectrosc.* **165**, 554–579 (1994).
[d] V. Boudon, F. Michelot, and J. Moret-Bailly *J. Mol. Spectrosc.* **166**, 449–470 (1994).