SYMMETRY-BASED TUNNELINGS IN HIGH-RESOLUTION ROVIBRATIONAL SPECTRA OF OCTAHEDRAL MOLECULES

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High-resolution spectra of spherical-top molecules are known to demonstrate rotational level clustering. This clustering is well described as a rotational phase-space effect[a]. Multiple equivalent phase-space regions allow tunneling and thus splitting of the rotational clusters[b]. So far this has been done with an ad hoc tunneling Hamiltonian. Similar splittings have been shown for low dimensional systems[c], also with an ad hoc parameterization. While ad hoc tunneling parameterization is simple to understand, it becomes extremely difficult to apply for higher symmetries and for locally low-symmetry clustering when many tunneling paths are possible. Symmetry-based parameterization mitigates this complication.

This presentation will discuss how symmetry-based tunneling is applied for octahedral molecules and demonstrate how local-C_1, C_2, C_3 or C_4 clusters may be evaluated perturbatively. Connections to non-rotational systems, such as large amplitude motion, will be discussed as well.

[a] W.G. Harter and C.W. Patterson, Phys Rev Lett 38, 224 (1977)
[b] W.G. Harter and C.W. Patterson, J Chem Phys 66, 4872 (1977)
[c] J.T. Hougen J Mol Spect 123, 197 (1987)