ROTATIONAL SPECTRA OF MOLECULES CONTAINING THREE METHYL TOPS: A COMPARATIVE STUDY OF $(CH_3)_3GeCl$ and $(CH_3)_3SnCl$

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The rotational spectra of C_{3v}–symmetric molecules $(CH_3)_3XCl$ with X=Si, Ge, and Sn are quite complicated exhibiting dense line patterns arising from internal rotation of the three methyl tops, the quadrupole coupling interaction of the chlorine atom, and the large number of isotopes. The MS group of such molecules is G_{162}[a]. A comparative analysis of the three rotational spectra of $(CH_3)_3XCl$ is especially interesting: While silicon and germanium are known to have very similar chemical and physical properties, tin behaves quite differently because d-orbitals are occupied only for Sn, which is also recognizable by the jump in their covalence radii (1.17 Å (Si), 1.22 Å (Ge), and 1.44 Å (Sn)). The barriers to internal rotation of the methyl tops bound to the central atoms can be expected to progress in an analogous way. In particular the increasing distance between hydrogen atoms of neighboring methyl groups, rising to about 3.8 Å for $(CH_3)_3SnCl$, implies a barrier to internal rotation introduced directly through the chemical bonding rather than from steric repulsion.
While the torsion-rotation analysis of $(CH_3)_3SiCl$ is straight forward[b] and closely follows local mode theory considering internal rotation of one top at a time, already $(CH_3)_3GeCl$ displays an altered splitting pattern which becomes severely complicated for $(CH_3)_3SnCl$. In addition, we observed a quadrupole splitting pattern and linear Stark-effect behavior for several $K = 0$ torsional species of $(CH_3)_3SnCl$, which we are hoping to explain with $\Delta K = \pm 1$–mixings.
To support the spectroscopic analysis of these spectra we worked out the Hamiltonian matrices for $K = 0$ and $K = 1$ in the high barrier group-theoretical tunneling-rotation formalism appropriate for the PI group G_{162}. For a physical understanding of the interesting tunneling phenomena, we are progressing towards an effective Hamiltonian for the different G_{162} torsional species, explicitly formulating $\Delta K = \pm 1$-coupling terms.

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[a] K. D. Möller and H. G. Andresen *J. Chem. Phys.* **39**, 17, 1963.
[b] I. Merke, W. Stahl, S. Kassi, D. Petitprez and G. Wlodarczak *J. Mol. Spectr.* **216**, 437, 2002.