ON THE METHYL INTERNAL ROTATION PROBLEM

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During internal rotation a group of atoms, called the top, rotates with respect to another group of atoms, called the frame. Research papers and textbooks addressing the problem of internal rotation, e.g., that of the methyl top, usually explain symmetry characteristics of the resulting torsional potentials by local geometrical symmetries of the molecule.
Recently we showed[a] how symmetry properties of torsional potentials derive from permutation-inversion symmetry and a peculiar nature of torsional dynamics. The same arguments prove that symmetry properties of torsional potentials have no relation to actual geometrical symmetries. Consequently, in all methyl internal rotation problems the torsional curves must have $2\pi/3$ periodicity, independently of the frame. First-principles validation is provided for the minimum energy torsional potential curves of ethane, acetaldehyde, and α-alanine. Experimentally relevant consequences of the computation of high-quality *ab initio* torsional potentials for acetaldehyde, incorporating effects due to special relativity and a first-order correction to the Born–Oppenheimer approximation, and for the three lowest-energy conformers of α-alanine are discussed in detail.

[a] V. Szalay, A. G. Császár, and M. L. Senent, J. Chem. Phys. 117, 6489 (2002).