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# SYMMETRY BEYOND PERTURBATION THEORY: FLOPPY MOLECULES AND ROTATION-VIBRATION STATES

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In the customary approach to the theoretical description of the nuclear motion in molecules, the molecule is seen as a near-static structure rotating in space. Vibrational motion causing small structural deformations induces a perturbative treatment of the rotation-vibration interaction, which fails in fluxional molecules, where *all* vibrational motions are large compared to the linear extension of the molecule. An example is protonated methane ($CH_5^+$) [a]. For this molecule, customary theory fails to simulate reliably even the low-energy spectrum. Within the traditional view of rotation and vibration being near-separable, rotational and vibrational wavefunctions can be symmetry classified separately in the molecular symmetry (MS) group [b]. In the present contribution we discuss a fundamental group theoretical approach to the problem of determining the symmetries of molecular rotation-vibration states. We will show that all MS groups discussed so far are subgroups of the special orthogonal group in three dimensions $SO(3)$ [c]. This leads to a group theoretical foundation of the technique of equivalent rotations [d]. The MS group of protonated methane ($G_{240}$) represents, to the best of our knowledge, the first example of an MS group which is not a subgroup of $SO(3)$ (nor of $O(3)$ nor of $SU(2)$). Because of this, a separate symmetry classification of vibrational and rotational wavefunctions becomes impossible in this MS group, consistent with the fact that a decoupling of vibrational and rotational motion is impossible. We want to discuss the consequences of this. In conclusion, we show that the prototypical floppy molecule $CH_5^+$ represents a new class of molecules, where usual group theoretical methods for determining selection rules and spectral assignments fail so that new methods have to be developed.

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[a] P. Kumar and D. Marx, Physical Chemistry Chemical Physics **8**, 573 (2006); Z. Jin, B. J. Braams, and J. M. Bowman, The Journal of Physical Chemistry A **110**, 1569 (2006); A. S. Petit, J. E. Ford, and A. B. McCoy, The Journal of Physical Chemistry A **118**, 7206 (2014).

[b] P.R. Bunker and P. Jensen, *Molecular Symmetry and Spectroscopy* (NRC Research Press, Ottawa, Canada, 1998).

[c] Being precise, we must include O(3) and SU(2), but our theory can be easily extended to these two groups.

[d] H. Longuet-Higgins, Molecular Physics **6**, 445 (1963).