SYMOMETRY BEYOND PERTURBATION THEORY: FLOPPY MOLECULES AND ROTATION-VIBRATION STATES

Conference Paper · June 2015
DOI: 10.15278/isms.2015.MI02

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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$_5^+$)\textsuperscript{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\textsuperscript{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)\textsuperscript{c}. This leads to a group theoretical foundation of the technique of equivalent rotations\textsuperscript{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.


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