

4th International Conference on

PHYSICAL AND THEORETICAL CHEMISTRY

September 18-19, 2017 Dublin, Ireland

*Per Jensen*

University of Wuppertal, Germany

Making headway in understanding the rotation-vibration spectrum of protonated methane CH_5^+ - an extremely flexible molecule

Traditionally, molecules are theoretically described as near-static structures rotating in space. Vibrational motion causing small structural deformations induces a perturbative treatment of the rotation-vibration interaction. This treatment fails in highly flexible molecules, where all vibrational motions have amplitudes comparable in size to the linear dimensions of the molecule. An example is protonated methane (CH_5^+). For these molecules, 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 wave functions are symmetry classified separately in the molecular symmetry (MS) group. All MS groups discussed so far are isomorphic to subgroups of the special orthogonal group in three dimensions SO. This leads to a group theoretical foundation of the technique of equivalent rotations. The group G_{240} (the MS group of protonated methane) represents, to the best of our knowledge, the first example of an MS group which is not isomorphic to a subgroup of SO. Because of this, a separate symmetry classification of vibrational and rotational wave functions becomes impossible in this MS group, consistent with the fact that a decoupling of vibrational and rotational motion is impossible. The talk will discuss the consequences of this and propose an alternative description making use of the fact that G_{240} and SO are both subgroups of the group SO of rotations in five-dimensional space. We take SO to be a near-symmetry group for CH_5^+ and develop a theoretical model that successfully explains recent experimental observations of rotation-vibration transitions in cold CH_5^+ . Two of the vibrational degrees of freedom are essentially free and, in an initial approximation, these vibrations are combined with the usual rotation in 3D space with the resulting motion being viewed as free rotation in 5D space, consistent with the symmetry group SO.

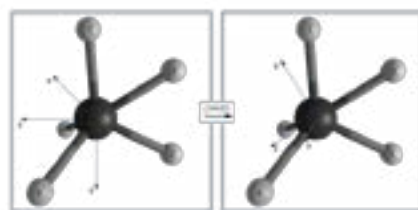


Figure 1: The effect of the proton permutation (15432) on a CH_5^+ ion. It rotates the quantization axis z and so the customary technique of equivalent rotations cannot be applied.

Biography

Per Jensen is a Professor of theoretical chemistry at University of Wuppertal, Germany. His research interests lie in "High-resolution molecular spectroscopy and quantum chemistry". He develops and applies methods for the accurate simulation of rotation-vibration spectra of small molecules, mostly of astrochemical and/or atmospheric interest. He is particularly interested in the application of molecular symmetry to facilitate the solution of nuclear-motion problems. Recently, he has worked extensively on interactions between electronic states (the Renner effect), the characterization of rovibrational energy clusters at high rotational excitation, and extremely flexible (structure-less) molecules. He is author and co-author of about 200 publications.

jensen@uni-wuppertal.de