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ON THE LOWEST RO-VIBRATIONAL STATES OF PROTONATED METHANE: EXPERIMENT AND ANALYTICAL MODEL

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Protonated methane, CH_5^+, is the prototype of an extremely floppy molecule. To the best of our knowledge all barriers are surmountable in the rovibrational ground state; the large amount of zero-point vibrational energy leads to large amplitude motions for many degrees of freedom. Low resolution but broad band vibrational spectroscopy [1] revealed an extremely wide range of C-H stretching vibrations. Comparison with theoretical IR spectra supported the structural motif of a CH_3 tripod and an H_2 moiety, bound to the central carbon atom by a 3c2e bond. In a more dynamic picture the five protons surround the central carbon atom without significant restrictions on the H-C-H bending or H_n-C torsional motions. The large-amplitude internal motions preclude a simple theoretical description of the type possible for more conventional molecules, such as the related spherical-top methane molecule. Recent high-resolution ro-vibrational spectra obtained in cold ion trap experiments [2] show that the observed CH_5^+ transitions belong to a very well-defined energy level scheme describing the lowest rotational and vibrational states of this enigmatic molecule. Here we analyse the experimental ground state combination differences and associate them with the motional states of CH_5^+ allowed by Fermi-Dirac statistics. A model Hamiltonian for unrestricted internal rotations in CH_5^+ yields a simple analytical expression for the energy eigenvalues, expressed in terms of new quantum numbers describing the free internal rotation. These results are compared to the experimental combination differences and the validity of the model will be discussed together with the underlying assumptions.

[1] O. Asvany, P. Kumar, I. Hegemann, B. Redlich, S. Schlemmer and D. Marx, Science **309**, (2005) 1219-1222
[2] O. Asvany, K.M.T. Yamada, S. Brünken, A. Potapov, S. Schlemmer, Science **347** (2015) 1346-1349