DOES CH_5^+ HAVE A STRUCTURE?

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CH_5^+ has presented a long-standing set of challenges from both a theoretical and experimental prospective. While it is recognized that this molecular ion plays an important role in interstellar and combustion chemistry, the measurement and assignment of a high-resolution laboratory spectrum have proven to be extremely challenging. Part of the challenge comes from the fact that there are 120 equivalent minima on the potential surface and the barriers separating the minima are no more than 300 cm^{-1}, while the zero-point energy of CH_5^+ is roughly 11 000 cm^{-1}. Recently, Brown, et. al. developed a potential surface for CH_5^+ that accurately reproduces their calculated *ab initio* points, obtained using a MP2/cc-pVTZ level of theory/basis, up to 14 000 cm^{-1}.[a] More recently, this surface has been extended to higher energies.

In this talk, we report the results of recent studies of the ground state properties of CH_5^+ and its partially dueterated isotopomers. We use Diffusion Monte Carlo approaches to obtain the ground state wave function, probability density and zero-point energy, as well as properties of selected low-lying vibrationally excited states. The probability densities are analyzed to determine the extent to which this molecular ion exhibits a well-defined structure. Based on these studies, it is found that the ground state of CH_5^+ is fully delocalized across all of the minima and has amplitude at configurations that correspond to the position of the barriers between the minima. Partial deuteration of the ion tends to localize the ground state wave function into a fraction of the energetically accessible configuration space.

[a] A. Brown, B. J. Braams, K. M. Christoffel, Z. Jin, and J. M. Bowman, J. Chem. Phys. 119, 8790 (2003).