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Probing CH_5^+ ions via collisions in rf guides and traps

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The structure of CH_5^+, the prototype of hypercoordinated carbocations, is still a mystery. In recent years, many efforts in spectroscopy, theory, and collision dynamics have contributed several pieces to the puzzle but there is no final answer to the question whether there are isomers separated by high enough barriers to be of practical importance or whether there is just an arrangement of five equivalent H-atoms, even at temperatures of a few K. The infrared spectra of CH_5^+ measured near 3000 cm^{-1} are still waiting to be assigned.[1] The predissociation spectra have provided interesting information on $(CH_5^+)(H_2)_n$ clusters; however, it must be expected that the ligands - although only weakly interacting - change the structure of the central CH_5^+ ion. While recent sophisticated quantum chemistry calculation indicate that it is a fluxional molecule, also if one or several protons are substituted by deuterons, ICR experiments[1] seem to provide evidence that one can create stable $[CH_3{\cdot}HD]^+$ isotopomers via deuteron transfer from CD_4^+ to CH_4. The 1 : 1 ratio of proton to deuteron transfer to NH_3 was taken as a hint that only the "HD-molecule" participates while the three *H* atoms in the (3c-2e) bonds do not contribute to NH_4^+ production.[1]

In this contributions we will illustrate the potential and the limitations of detailed collision experiments in finding correlations between structure and reactivity. All examples presented are related to protonated methane and deuterated variants, *e.g.*, formation of CH_5^+ via $CH_4^+ + CH_4$, $CH_4^+ + H_2$, or radiative association of $CH_3^+ + H_2$, modification by H- D scrambling or destruction of CH_5^+ via a collision with H. The experiments have been performed using rf ion guides and ion traps.[2-4] Integral and differential cross sections measured for $CH_4^+ + CH_4$ / CD_4 collisions in a GIB-TOF arrangement indicate that CH_5^+ formation is more complicated than just a simple proton transfer. Careful studies of CH_5^+ + HD in the 15 K trap revealed that there is no H- D exchange at all. Very recently, also first measurement of CH_5^+ + D have been made in a new trapping machine indicating that CH_4D^+ formation is slow, if it occurs at all.[5] So far our results indicate that it is complicated to get information on the structure of CH_5^+ from reaction dynamics. Nonetheless isotope scrambling at low temperature is a very sensitive probe but a careful interpretation has to account for differences in zero point energies, also in transition states, and restrictions imposed by symmetry selections rules.

A new generation of experiments which is in preparation combines an ion trap operating at a few K (or below) and H-atom beams for chemical probing with suitable lasers including IR and FIR. The method of laser induced reactions (LIR) will provide simultaneously state specific reaction rate coefficients and excitation wavelength of well-prepared, very cold ions. It can be foreseen that such detailed data will tell us whether the picture of five equivalent protons swarming around the central carbon is correct.

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3 D. Gerlich, *Applications of rf fields and collision dynamics in atomic mass spectrometry,* J. Anal. At. Spectrom., **19** (2004) 581.
4 O. Asvany, I. Savic, S. Schlemmer, D. Gerlich, *Variable temperature ion trap studies of $CH_4^+ + H_2$, HD and D_2*, Chem. Phys. **298** (2004) 97.
5 G. Borodi, A. Luca, D. Gerlich, *Probing protonated methane, CH_5^+, with H and D-atoms*, in preparation