Does CH_5^+ Have (a) "Structure?" A Tough Test for Experiment and Theory**

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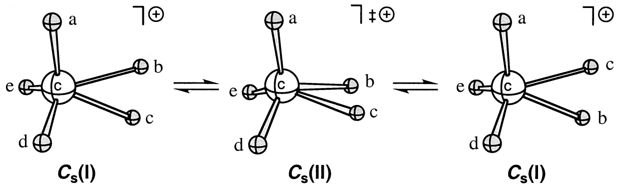
In a very naive view, the notion of structure seems like a fundamental law of physics: atoms bond together to form molecules in regular, predictable ways. This quasi-classic framework, however, is not supported in the sense of strict quantum mechanics, and is only possible if one assumes the separation of nuclear and electronic motion (Born–Oppenheimer approximation) which forms the necessary hirarchy to describe the "structure" of a system within classic observables.[1] Although many molecules exist in isomeric forms, chemists mostly refer to the structure of a compound as the geometrical isomer lowest in energy. But what happens if other isomers (or stationary structures) are energetically very close and the barriers for their interconversion are small so that there is practically no preference, even at the lowest achievable temperatures? This situation arises for the methonium ion, CH_5^+, whose three lowest lying stationary structures are nearly degenerate and equilibration of the minima is facile (barriers < 1 kcal mol^{-1}), even at 0 K. The recently reported high-resolution infrared spectrum of this enigmatic species by Oka et al.[2] seems to confirm theoretical predictions that this molecule is highly fluctional and that the term "structure" may have to be refined for CH_5^+.[3–5]

The methonium ion is the smallest protonated alkane and was suggested by Olah et al. as the prototype for the entire group of nonclassical carbonium ions, which play important roles as intermediates in acid-catalyzed transformations of hydrocarbons and in many electrophilic reactions.[6] Hence, the significance of the structure of this ion is that it is the cornerstone for mechanistic proposals for these and related transformations.[7, 8] The methonium ion is also of astrochemical interest as it may serve as a spectroscopically sensitive indicator for the abundance of methane in cold interstellar clouds.

Although CH_5^+ was discovered as early as 1952 by Tal'roze and Lyubimova in mass spectrometric studies,[9] where it is still used to date as an agent for chemical ionization, its geometry has never been determined experimentally. As a matter of fact, the five hydrogen atoms around CH_5^+ were considered equivalent[10] before the advent of the first insightful theoretical predictions in the late 1960s and early 1970s by the groups of Kutzelnigg, Pople, and others.[11–15] These studies suggested that CH_5^+ consists of a pyramidalized CH_3^+ unit strongly bound ($D_o = 40-45$ kcal mol^{-1})[16, 17] to an H_2 molecule, resulting in a formal three-center, two-electron bonding arrangement which is at the heart of Olah's electrophilic carbonium ion chemistry.[8] One of the two resulting C_s-symmetric structures is the global minimum, $\boldsymbol{C_s}$**(I)**, whereas the other, $\boldsymbol{C_s}$**(II)**, is a transition structure for the rotation of the H_2 moiety (Scheme 1) which is associated with an extremely low barrier at all levels of theory (around 0.1 kcal mol^{-1}). There are also C_{4v} and D_{3h} forms which are higher order stationary points meaning that they are chemically not very meaningful.[18]



Scheme 1. The computed global CH_5^+ minimum, $\boldsymbol{C_s}$**(I)**, and the transition structure for the H_2-rotation, $\boldsymbol{C_s}$**(II)**.

A second, C_{2v}-symmetric transition state, which does not display a recognizable H_2 subunit,[13] is responsible for exchanging the protons of the H_2 moiety with those of the CH_3^+ tripod (Scheme 2). Hence, the relative energy of the C_{2v} structure determines whether CH_5^+ is indeed the nonclassical carbonium ion prototype, that is, whether the barrier is sufficiently high or whether all C–H bonds are statistically averaged in the case of a vanishingly low energy of this transition structure. This is when the situation becomes challenging for experiment and theory, as it is increasingly difficult to resolve the spectral data and to determine the relative energies of a molecule with decreasing barriers for interconversion of low-lying minima.

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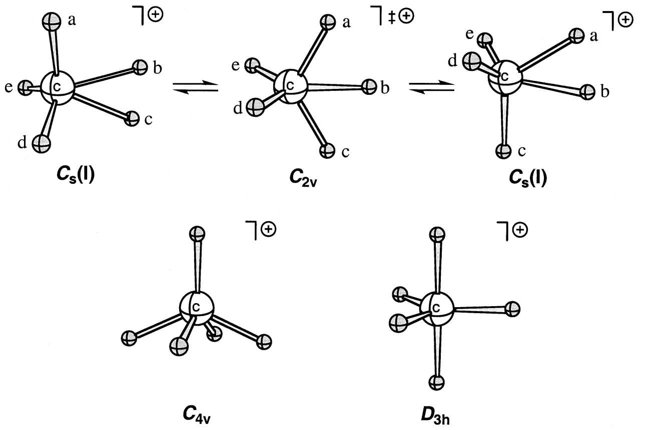

Scheme 2. The exchange (via transition structure $\boldsymbol{C_{2v}}$) of equivalent protons in CH_5^+ ($\boldsymbol{C_s}$**(I)**) and the higher order (i.e., nonminima) stationary structures with C_{4v} and D_{3h} symmetry.

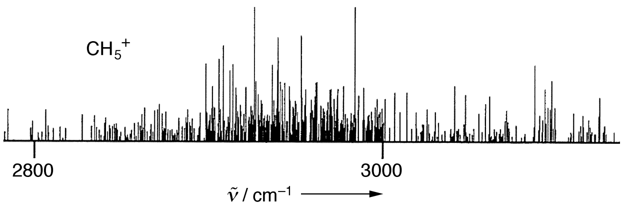

Figure 1. High-resolution IR spectrum of CH_5^+. (Reproduced with permission from T. Oka).

The C_{2v} barrier is very sensitive to electron correlation treatment and the size of the basis set.[19] Improvement in the sophistication of the theoretical treatment, for instance, by using the highly correlated coupled-cluster approach[20] in conjunction with very large basis sets lowers the C_{2v} barrier to less than 1 kcal mol^{-1}.[3, 5] As the zero-point vibrational energy (ZPVE) correction is of similar magnitude, it appears that proton scrambling occurs essentially freely, even at 0 K. In practical chemical terms, this was expressed in calling the methonium ion *unique* rather than serving as the nonclassical carbonium ion prototype.[3, 4] Kutzelnigg et al., however, pointed out that the use of harmonic ZPVE corrections may not be entirely correct for energetically very close-lying stationary points. [5]

This classical quantum-mechanical analysis was both supported and criticized by highly elaborate density functional calculations which take into account the dynamics of the system in the sense of quantum-statistical mechanics.[21] Here it was found that CH_5^+ undergoes large-amplitude pseudorotations, which result in hydrogen scrambling and statistically equivalent protons. Nevertheless, there is a high probability of finding structures akin to the classical $\boldsymbol{C_s}$**(I)** quantum ground state. Parrinello referred to this situation as an "intramolecular liquid" where the protons move, but in a highly correlated way that preserves local structure.[22] Such a situation can then only be defined in a statistical sense using distribution functions rather than by assigning atomic coordinates. Clearly, this is an uncomfortable situation for chemists who require that a stable molecule, which CH_5^+ obviously is with respect to dissociation and deprotonation, must have (a) structure.[23] A possible solution of this dilemma may be offered by Marx and Savin who demonstrated that a topological analysis of the electron localization function (ELF) of representative configurations including tunneling and zero-point vibrational effects is useful in extracting structure even from highly fluctional molecules.[24] Such an analysis also suggests that CH_5^+ is indeed very floppy but shows considerable statistical preference for $\boldsymbol{C_s}$**(I)**-like structures.

The recently reported experimental IR spectrum of CH_5^+ by Oka et al. (Figure 1),[2] a major achievement in high-resolution infrared spectroscopy, allows a first experimental analysis of the theoretical predictions. Although it is relatively easy to generate CH_5^+ by means of electron impact ionization of methane [Eq. (1)] or by proton transfer [Eqs. (2) and (3)],

$$CH_4^{+\bullet} + CH_4 \longrightarrow CH_5^+ + {}^\bullet CH_3 \tag{1}$$

$$H_2^{+\bullet} + H_2 \longrightarrow H_3^+ + H^\bullet \tag{2}$$

$$H_3^+ + CH_4 \longrightarrow CH_5^+ + H_2 \tag{3}$$

the experimental setup to record a resolved IR spectrum is rather demanding because the resolution is highly dependent on the dimensions of the discharge tube, the energy of the laser system, the gas-mixing ratios of H_2 and CH_4 (50:1 in the experiment reported by Oka et al.), and the total pressure. Despite extensive efforts by the top practitioners, the spectrum in question had never been resolved due to the apparent fluctionality of the methonium ion.[25]

The groups of Hiraoka[26] and Lee[27] used a limited number of "solvent" molecules {CH_4 and $(H_2)_n$; $n = 1-6$} to slow down the rate of hydrogen scrambling. In spite of the stabilizing effect when attaching just one H_2 to CH_5^+, the IR spectrum remains unresolved due to strong anharmonic couplings among vibrational modes.[27, 28] With three hydrogen molecules attached, the CH_5^+ core becomes semirigid and allows some interpretation of the corresponding IR spectrum. However, as these approaches strongly influence the energetics and structures of the target molecule, none of them can claim to have resolved the vibrational bands of unperturbed CH_5^+.

Oka's spectrum consists of about 900 spectral lines in the narrow region of 3150–2770 cm^{-1} (Figure 1), but appears to be significantly different from other close-lying absorptions due to other species and possibile impurities. As the experimental spectrum is extremely complicated and does not show regularity or symmetry, it supports the collective theoretical evidence on the highly fluctional nature of CH_5^+. The answer to the crucial question whether a preference for the C_s(I) quantum ground state exists,[29] must await the assignment of the experimental absorptions. This will probably require that the IR spectrum be recorded at very low temperatures and that the spectra of isotopomers be used as additional sources of information. From a theoretical point of view, accurate full ab initio potentials and variational calculations are needed but will require much more powerful computers than available today. The theoretically carefully elaborated rotational spectrum of CH_5^+ also still awaits its experimental realization.[30–32] This fascinating story continues.[33]

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Organometallic Transformations Demonstrate That Fluorocarbons Are Reactive Molecules

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Fluorine forms the strongest single bond to carbon. The great strength of this bond, along with the small size and high electronegativity of fluorine, conspire to give rise to the unusual properties associated with highly fluorinated organic molecules.[1] Indeed, the most characteristic chemical property of fluorocarbons is their *lack* of reactivity. The stability imparted by the C–F bond leads to the long atmospheric lifetimes of chlorofluorocarbons (CFCs); saturated perfluorocarbons (PFCs) are even more stable, with CF_4 having an estimated stratospheric lifetime of more than 10000 years.[2]

The unique properties of fluorinated groups have long been exploited by organometallic chemists to stabilize unusual molecules and provide a benchmark for comparisons with analogous hydrocarbon ligands.[3, 4] Current activity has focused on the preparation of highly fluorinated ligands that contain "fluorous ponytails". These "ponytails" impart solubility in PFC solvents, a property which is necessary for application in "fluorous" biphase chemistry.[5] This technique exploits the unusual solubility properties of PFCs to address the technologically important problem of the separation of PFC-containing catalysts or reagents from hydrocarbon-soluble products. Clearly the success of this strategy requires that the PFC phase remains inert under the reaction conditions. This article will trace recent developments in the reaction chemistry of saturated PFCs and PFC ligands in organometallic complexes with an emphasis on how organometallic reagents enable transformations to be performed under remarkably mild conditions.[6]

The advances in the reaction chemistry of totally saturated PFCs and CFCs with special focus on the defluorination chemistry were summarized by Saunders in 1996.[7] Strong reducing agents mineralize PFCs and CFCs but partial and selective C–F activation has been achieved under homogeneous conditions with the sodium benzophenone radical anion or with cobaltocene in the presence of lithium trifluoromethanesulfonate.[8] Metal–organic electron donors have been applied to the synthesis of organofluorine compounds (Scheme 1).[9]

Catalytic defluorination chemistry has been achieved utilizing early transition metallocenes ($[Cp_2TiF_2]$, $[Cp_2ZrCl_2]$)

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