

Density Functional Theory and Complete Basis Set *Ab Initio* Computational Study of Five-, Six-, Seven- and Eight-hydrogen Coordinated Carbon Cations†

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High level *ab initio* and density functional theory studies are performed on highly protonated methane species.

It was Olah's extensive studies that pointed out that two-electron three-centered bonding is possible in the explanation of the existence of hypervalent carbon atom in protonated hydrocarbons¹ and established the concept that carbon is not limited in bonding to only four atoms or groups.² The CH_5^+ ion considered as the parent of non-classical carbocations, containing a five-coordinate carbon atom.³ From recent Car-Parrinello *ab initio* simulation and Kutzelnigg's CCSD(T)-R12 calculation,⁴ it was concluded that CH_5^+ has C_s symmetry,⁵ which was previously suggested by Olah.⁶ There are also some computational studies that support the existence of doubly and triply protonated methane.⁷ Experimental confirmation of CH_5^+ in the gas phase comes from IR spectroscopy⁸ and from Fourier transform ion cyclotron resonance mass spectrometry.⁹ In the latter experimental study, all data can be explained with the C_s structure of CH_5^+ . A firm suggestion that hypervalent carbon can exist comes from organometallic compounds, which are even stable enough

to survive an X-ray crystallographic study. For instance, Schmidbaur has isolated and determined the structure of mono-positive gold complex $[(\text{Ph}_3\text{PAu})_5\text{C}]^+$, an analog of CH_5^+ .¹⁰

Here, we present a computational study for structural and energetic properties of poly-protonated methyl radical and methane. First, let us explore structural properties for the highly coordinated carbonium ion computed at the MP2/6-31G(d') theory level (Fig. 1). There are three minima for the CH_5^+ structure, two of them have C_s symmetry, while one has C_{2v} symmetry. One would expect that the C–H bond distances are slightly longer for all bonds than in methane (1.09 Å). However, all of these three structures have at least two C–H bond distances that are shorter than in methane, with two or three C–H bond distances longer than in methane. All positive charge is spread on the hydrogen atoms with higher density on the hydrogen with the longest C–H bond distance. This conclusion is obtained from every computational method, regardless of

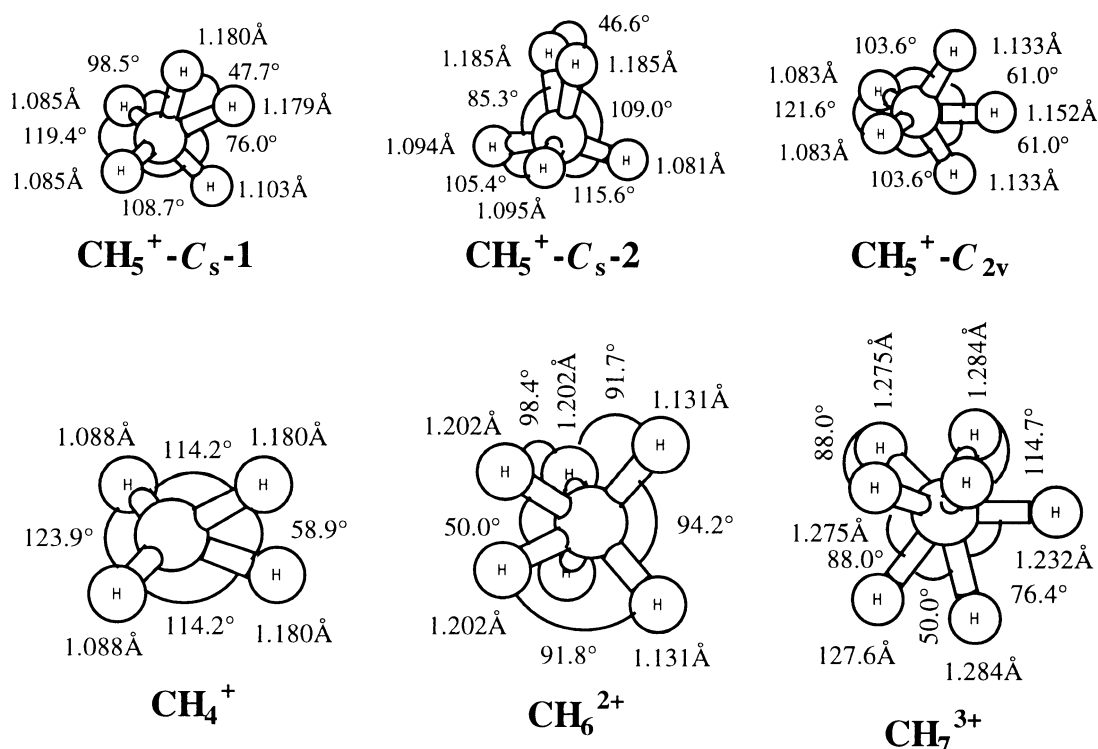


Fig. 1 The MP2/6-31G(d,p) structural parameters for lowest stationary points on the CH_5^+ potential energy surface and for CH_4^+ , CH_6^{2+} , CH_7^{3+} cations.

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whether it belongs to the *ab initio* or density functional theory family. Contrary to the CH_5^+ structures, only one structure for CH_4^+ , CH_6^{2+} and CH_7^{3+} was located on their potential energy surfaces. All of them have a common struc-

Table 1 Estimated energies (kcal mol⁻¹) for various protonated methyl radical and methane derivatives

Theory	$\Delta H(I)$	$\Delta H(II)$	$\Delta H(III)$	$\Delta H(IV)$	$\Delta H(V)$	$\Delta H(VI)$	$\Delta H(VII)$	$\Delta H(VIII)$
MP2	0.10	0.93	-40.7	-125.9	50.6	64.0	14.6	247.5
CBSQ	0.11	0.13	-39.7	-127.9	34.5	63.5	20.4	242.8
B3LYP	-0.08	-0.49	-41.6	-129.8	38.2	61.5	24.2	241.3
BLYP	-0.05	-0.58	-42.7	-130.9	36.7	60.2	25.9	240.0
Est.	0.10	0.82	-42.0	-129.4				
Exp.			-42.5	-130.2				

$\Delta H(I)$ = relative energy of CH₅⁺-C_s-2 conformer relative to the CH₅⁺-C_s-1 conformer; $\Delta H(II)$ = relative energy of the C_{2v}CH₅⁺ conformer relative to the CH₅⁺-C_s-1 conformer; $\Delta H(III)$ = enthalpy for the reaction CH₃⁺ + H₂ → CH₅⁺; $\Delta H(IV)$ = enthalpy for protonation of CH₄; $\Delta H(V)$ = enthalpy for the reaction CH₄ + H₃O⁺ → CH₅⁺ + H₂O; $\Delta H(VI)$ = enthalpy of protonation of CH₅⁺; $\Delta H(VII)$ = enthalpy for the reaction CH₄⁺ + H₂⁺ → CH₆²⁺; $\Delta H(VIII)$ = enthalpy of protonation of CH₆²⁺.

tural feature, they can be very easily envisioned as a product of a proton insertion into their neutral precursors (methyl radical and methane). All of these bonds are three-centered two-electron aromatic systems. In these bonds the C-H bond distance is slightly longer than the non-protonated C-H bond. In general, these structures are what can be expected on the basis of some previous computational studies.⁴⁻⁶

Let us now evaluate the relative energies for three different CH₅⁺ conformers (Table 1). It was estimated that the most stable is the conformer CH₅⁺-C_s-1 (Fig. 1). All *ab initio* studies predict that the other two conformers have higher energy and the estimated energies agree well with each other. These results are in contradiction with the DFT computed energies. Both hybrid and gradient DFT methods suggest that CH₅⁺-C_s-2 is the most stable CH₅⁺ conformer. Considering the fact that the energy differences are very small and that the accuracy of the DFT methods is at best ±2.0 kcal mol⁻¹, these results are not reliable. Our CBSQ energies are probably the most accurate values that predict the CH₅⁺-C_s-1 isomer as the most stable. There are several ways that CH₅⁺ can be prepared. One of them is through the reaction CH₃⁺ + H₂ → CH₅⁺ and the estimated enthalpy for this reaction is -42.5 kcal mol⁻¹.¹¹ Both hybrid B3LYP and gradient BLYP DFT methods reproduce this value well (Table 1). CH₅⁺ can also be prepared by the protonation of methane by a super acid. Again, the DFT estimated enthalpy of methane protonation agrees well with high *ab initio* energy value and it is almost identical to the experimental value (Table 1). If water is present, even in trace amounts, this protonation will not occur since the enthalpy for proton transfer from H₃O⁺ to methane is estimated to be ca. 35.0 kcal mol⁻¹ [$\Delta H(V)$, Table 1].

CH₆²⁺ can be prepared through a one step double protonation of methane, through single protonation of CH₅⁺, or through the reaction CH₄⁺ + H₂⁺ → CH₆²⁺. It was already computed that the first protonation of methane is an exothermic reaction. If two protons are to be introduced simultaneously, then the reaction is predicted to also be exothermic (68.3 kcal mol⁻¹ at B3LYP theory level). If the reaction occurs in two steps then the second step, *i.e.* of CH₅⁺ protonation is endothermic (61.5 kcal mol⁻¹ at the B3LYP theory). The same is true, although with lower energy demand for the reaction CH₄⁺ + H₂⁺ → CH₆²⁺. The enthalpy of the reaction is 24.2 kcal mol⁻¹ at the B3LYP level (Table 1).

Optimized structures of even more highly protonated methane is computationally very difficult. It does not come as a surprise that for the protonation of CH₆²⁺ with the for-

mation of CH₇³⁺ the enthalpy is estimated to be endothermic at 241.3 kcal mol⁻¹ (Table 1). This energy is exceptionally high and we anticipate that experimental preparation of this molecular species would be very difficult, if not impossible. For CH₈⁴⁺ it was not possible to locate any minimum on its potential energy surface.

From the results presented here it is obvious that the CBSQ, hybrid B3LYP and gradient corrected BLYP density functional theory method computed energies are very close to some available experimental data. It was predicted that CH₅⁺ with C_s symmetry should be possible to prepare in the gas phase or in the condensed phase of a super acid from methane and the proton, or from the methyl radical and hydrogen cation. On the other hand, CH₆²⁺ is a very unstable molecule, and if prepared, should readily decompose. Higher protonated analogues of methane are predicted to be unstable and difficult to prepare.

Computational Methods.—All computational studies were performed with Gaussian 94 computational package and reported energies are estimated at 0 K. *Ab initio* energies are obtained as a single point CBSQ calculation on the MP2/6-31G(d,p) structures. For density functional methods hybrid B3LYP and gradient corrected BLYP methods in combination with 6-311G(2d,2p) basis set were used.¹²

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