Inter/intramolecular Bonds in TH₅⁺ (T = C/Si/Ge): The Uniqueness of Carbon bonds in Tetrel Bonds

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Abstract

Atoms in Molecules (AIM), Natural Bond Orbital (NBO), and normal coordinate analysis have been carried out at the global minimum structures of TH₅⁺ (T = C/Si/Ge). All these analyses lead to a consistent structure for these three protonated TH₄ molecules. The CH₅⁺ has a structure with three short and two long C-H covalent bonds and no H-H bond. Hence, the popular characterization of protonated methane as a weakly bound CH₃⁺ and H₂ is inconsistent with these results. However, SiH₅⁺ and GeH₅⁺ are both indeed a complex formed between TH₃⁺ and H₂ stabilized by a tetrel bond, with the H₂ being the tetrel bond acceptor. The three-center-two-electron bond (3c-2e) in CH₅⁺ has an open structure, which can be characterized as a V-type 3c-2e bond and that found in SiH₅⁺ and GeH₅⁺ is a T-type 3c-2e bond. This difference could be understood based on the typical C-H, Si-H, Ge-H and H-H bond energies. Moreover, this structural difference observed in TH₅⁺ can explain the trend in proton affinity of TH₄. Carbon is selective in forming a ‘tetrel bond’ and when it does, it might be worthwhile to highlight it as a ‘carbon bond’.
1. Introduction

The structure of a molecule provides valuable insights into its properties. CH$_5^+$ though, has gained notoriety for eluding a formal definition of its structure. Since its discovery in 1952 in mass spectrometric experiments [1], attempts at assigning this molecule with a definite structure have proved to be futile. This is because CH$_5^+$ is highly fluxional with theoretical investigations revealing that the potential energy surface (PES) is quite shallow [2,3]. The PES of CH$_5^+$ is characterized by 120 equivalent minima which are easily accessible via low lying saddle point structures [4–6]. The difference in energy between these saddle point structures and the C$_s$ symmetry minima is small and decreases with increasing levels of theory [7,8]. Though there is a consensus that the molecule is highly fluxional and the ground state minimum has C$_s$ symmetry, results regarding the C$_s$ symmetry minimum veer between a structure having a pentacoordinated carbon center with no interaction between the H atoms [9,10] and a structure where CH$_5^+$ is made up of a methyl cation (CH$_3^+$) complexed with H$_2$. [11,4,12] The crux of the matter then is, whether H$_2$ retains its identity in the molecule or not.

The nature of bonding in CH$_5^+$ can also be examined by studying the possible weak interactions that could lead to its formation. It is known that the hydrogen bonded structures are intermediates in proton transfer reactions. The hydronium ion (H$_3$O$^+$) and ammonium ion (NH$_4^+$) are formed by the protonation of H$_2$O and NH$_3$, respectively. These are often mediated by a hydrogen bonded complex such as H$_2$O⋯HX or H$_3$N⋯HX. Rotational spectroscopic investigations on several CH$_4$⋯HX (X= F, Cl, CN, and OH) dimers [13–15] reveal that the global minimum structure is the one where HX is the hydrogen bond donor and CH$_4$ is the acceptor. The H atom of HX forms a hydrogen bond with the carbon center through the tetrahedral face of CH$_4$. It has been pointed out that this hydrogen bonded structure having a ‘pentacoordinate carbon’ could be a precursor to the formation of CH$_5^+$ [16]. The three O-H bond lengths in H$_3$O$^+$ are equal and the same is true for the four N-H bonds in NH$_4^+$. If one were to guess the geometry of CH$_5^+$, without any prior knowledge, a trigonal bipyramidal would be a reasonable choice. Even in this structure, one would expect two long C-H bonds in the opposite directions and three short C-H bonds in a plane, such as in Fe(CO)$_5$ which is also a fluxional molecule. However, the established structure for CH$_5^+$ has C$_s$ symmetry with three short C-H bonds in one side (not in the same plane) and two long C-H bonds in the opposite side. It appears as though the H$_2$ moiety is separated from the CH$_3^+$ tripod. This arrangement then is reminiscent of a ‘carbon (tetrel) bond’ [17,18], which was proposed recently. The positively charged central carbon can accept electron density from the sigma electrons of H$_2$ forming a tetrel bonded complex. If such is the case then, a normal mode analysis on CH$_5^+$ could reveal H-H vibration and the vibrational frequency could show a red-shift. Moreover, Atoms in Molecules (AIM) and Natural Bond Orbital (NBO) theoretical analysis could yield evidence for the carbon bond.

The infrared spectrum obtained by Oka and coworkers [9] was an important step towards solving the structure of CH$_5^+$. The spectrum is complicated, with nearly 900 lines that depend on CH$_5^+$. However, none of these spectral lines could be assigned. In subsequent years, efforts were made to decipher this spectrum by obtaining another extended spectrum [12], by computing the spectrum using quantum calculations [5] and by obtaining the spectrum at low temperatures [19]. However, recent tentative assignments using combination differences by Asvany et al. [19] from the low temperature spectra and the calculated rotation- bending energy levels which were compared with this spectra [20] are the
closest one has come to solving the structure. This study could not give any information about H-H vibration in CH$_5^+$. Bader [21] opines that a distinction must be made between the molecular geometry and its structure, as molecular geometry is a non-generic property of the molecule defined by a set of nuclear coordinates, whereas, structure is a generic property defined by the network of bonds between atoms in a molecule. He notes that the “difficulties ascribed to the notion of molecular structure are the inabilities to assign a single geometrical structure...to a molecule in a ‘floppy' state wherein the nuclear excursions cover a wide range of geometrical parameters.” Bader proposed the use of the charge density topology of a molecule, to determine linkages of the atoms present. This is used to assign a molecular graph which defines the molecular structure. Therefore, the structure of CH$_5^+$ could be defined by performing a topological analysis of the electron density. Okulik et al. have in fact carried out a topological analysis of the electron density on the CH$_5^+$ molecule and concluded that it is a pentacoordinated carbocation with no interaction present between the H atoms [10] thereby providing evidence against the structure of CH$_5^+$ being a complex between CH$_3^+$ and H$_2$. Earlier studies by Marx and Savin, subjected CH$_5^+$ to a similar analysis, using the electron localization function (ELF), which is a local measure of the Pauli repulsion [22]. This helps locate regions having a pair of electrons. Their findings lead to four basins, three for the 2c-2e C-H bonds and one for the 3c-2e bond involving the H$_2$ moiety. This does not answer the question about whether or not there is H-H bond. Asvany et al. depict the structure of CH$_5^+$ with a 3c-2e bond with the H atoms of the H$_2$ moiety connected [19], whereas the molecular graph for CH$_5^+$ clearly shows no interaction between the H atoms (Figure 1). The question we then ask is, what does the molecular graph for the congeners of CH$_5^+$, SiH$_5^+$ and GeH$_5^+$ look like? Would this comparison help in choosing the right structure for CH$_5^+$?

![Figure 1](image-url)  
Figure 1. (a) Molecular graph for CH$_5^+$; (b) CH$_5^+$ as depicted in Reference 19.

Considering the difficulty in defining a structure for CH$_5^+$ it is interesting to examine the structures of SiH$_5^+$ and GeH$_5^+$. Are they similar, considering they belong to the same group or different? SiH$_5^+$ was first observed in ionized silane-methane mixtures using mass spectrometry by Beggs and Lampe [23]. The optimized geometries and the heats of hydrogenation for SiH$_3^+$ led Schleyer et al. to surmise that SiH$_5^+$ is a weakly bound complex of SiH$_3^+$ and H$_2$ [24]. The rovibrational spectrum of SiH$_5^+$ obtained by Boo and Lee provides evidence for the H$_2$ moiety rotating freely with respect to the SiH$_3^+$ frame [25].
GeH₅⁺ on the other hand was difficult to obtain and was first observed in ion beam scattering experiments by Senzer and coworkers [26]. Kohda-Sudoh et al. described the shape of GeH₅⁺ to be a loose complex between the germyl cation (GeH₃⁺) and H₂ [27]. The comprehensive study of all the structures of the GeH₅⁺ by Schreiner et al. concluded that the geometry having C₃v symmetry was the minimum on the potential energy surface [28]. It is evident that the ground state minimum structure for the TH₅⁺ molecule has C₃v symmetry.

Theoretical and spectroscopic results for SiH₅⁺ and GeH₅⁺ suggest that these are weakly bound complexes of the TH₃⁺ (T= Si, and Ge) cation with H₂. The topological analysis of the charge density would then allow us to observe a tetrel bonded interaction between the TH₃⁺ cation and the H₂ moiety. This has not been carried out so far to the best of our knowledge. In this work we compare the electron density topologies of SiH₅⁺ and GeH₅⁺ with CH₅⁺ and investigate if there is any evidence for a tetrel bond. Natural bond orbital theory and normal mode analysis on these structures have been carried out as well. This has helped in arriving at unambiguous conclusions about the structure of CH₅⁺. The results are presented here.

2. Computational methods

The geometries of the TH₅⁺ species (T= C, Si, and Ge) were optimized at the MP2 level of theory with the aug-cc-pVTZ basis set. Frequency calculations were also performed to ascertain the nature of the optimized geometries. The absence of an imaginary frequency confirms a structure to be a minimum and its presence indicates that the structure is a saddle point on the potential energy surface. The harmonic frequencies were also calculated using the B3LYP functional with the same basis set.

Relaxed potential energy scans were carried out by varying the distance between the TH₃⁺ moiety and H₂. This was computed using the keyword opt=modredundant. This allows all the parameters defining the molecule to alter during a scan. All calculations were performed using the Gaussian 09 suite of programs [29].

To establish the nature of bonding, the topological analysis of the electron density for the optimized structures of the TH₅⁺ was done using the AIMAll software [30]. It was also analyzed at select points of the potential energy scans to study the appearance or disappearance of various weak interactions and their role in the formation of the TH₅⁺ species. The wave function required for this calculation was obtained from the Gaussian computation at MP2/aug-cc-pVTZ level. The presence of the 3c-2e bonds and the nature of the bonding orbitals involved in the TH₅⁺ species were analyzed using NBO6.0 as implemented in Gaussian 09 [31].

3. Results

3.1. Optimized geometries

3.1.1 CH₅⁺

Methane distorts to accommodate the presence of the added proton to form CH₅⁺. The CH₅⁺ molecule was optimized at MP2/ aug-cc-pVTZ. The three lowest energy stationary structures obtained are shown below in Figure 2. The geometry with C₃v(I) symmetry is a minimum on the potential energy surface which is confirmed by the vibrational frequency analysis. The CH₅⁺ unit of the
molecule is more pyramidal than planar. Thus, CH$_{5}^{+}$ bears resemblance to a protonated methane structure rather than to a planar methyl cation (CH$_{3}^{+}$) interacting with an elongated H$_{2}$ molecule.

Figure 2. Optimized geometries and relative energies of three lowest energy stationary structures of CH$_{5}^{+}$ calculated at MP2/aug-cc-pVTZ. Number in brackets denotes number of imaginary frequencies.

A quantitative evaluation of the bond lengths reveals the presence of three short C-H bonds comprising the CH$_{3}$ tripod and two long C-H bonds which make up the H$_{2}$ moiety. These two C-H bonds are about 0.1 Å longer than the three other C-H bonds. Therefore, it appears as though the H-atoms involved in the long C-H bonds are a separate entity with respect to the CH$_{3}$ tripod. One of the three short C-H bonds is slightly longer (marked b in Figure 3) and it is with respect to this unique bond that the H$_{2}$ unit is eclipsed in the C$_{5}$ (I) geometry. The distance between the H atoms in the H$_{2}$ moiety is 0.9748 Å. When compared to the H-H distance in free H$_{2}$, which is 0.7374 Å, it seems that this bond is quite elongated with possibly no interaction between the H atoms. The C-H and H-H bond lengths are summarized in Tables 1 and 2.

Figure 3. The different T-H bonds in TH$_{5}^{+}$
Table 1. Bond lengths calculated at MP2/aug-cc-pVTZ

<table>
<thead>
<tr>
<th>Molecule</th>
<th>a(Å)</th>
<th>b(Å)</th>
<th>c(Å)</th>
<th>d(Å)</th>
<th>H-H (Å)</th>
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<tr>
<td>CH₅⁺</td>
<td>1.0852</td>
<td>1.1072</td>
<td>1.1835</td>
<td>1.1819</td>
<td>0.9748</td>
</tr>
<tr>
<td>SiH₅⁺</td>
<td>1.4606</td>
<td>1.4626</td>
<td>1.8790</td>
<td>1.8842</td>
<td>0.7727</td>
</tr>
<tr>
<td>GeH₅⁺</td>
<td>1.4985</td>
<td>1.5002</td>
<td>1.9477</td>
<td>1.9532</td>
<td>0.7697</td>
</tr>
</tbody>
</table>

Table 2. Bond lengths calculated at MP2/aug-cc-pVTZ

<table>
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<tbody>
<tr>
<td>CH₄</td>
<td>1.0863</td>
<td>CH₅⁺</td>
<td>1.0867</td>
<td>H₂</td>
<td>0.7374</td>
</tr>
<tr>
<td>SiH₄</td>
<td>1.4788</td>
<td>SiH₅⁺</td>
<td>1.4618</td>
<td>GeH₄</td>
<td>1.5007</td>
</tr>
</tbody>
</table>

The second stationary structure is a saddle point on the potential energy surface, confirmed by the presence of an imaginary frequency. This structure has C₃(II) symmetry with the H₂ moiety staggered with respect to the unique C-H bond (b). The C₃(II) saddle point is the transition state for the rotation of the H₂ unit about the pseudo C₃ axis in the methanium ion as noted in earlier works [4-8]. The energies computed at MP2/aug-cc-pVTZ indicate that this structure is only 0.59 kJmol⁻¹ higher in energy with respect to the minimum C₃(I) structure. Therefore, the rotation of the H₂ moiety about the pseudo C₃ axis would be facile.

The third structure is also a saddle point on the potential energy surface. Three of the C-H bonds in this structure are in a plane and equidistant from each other. This C₃v symmetry structure is the transition state on the reaction coordinate where the H atom flips between the H₂ moiety and the CH₃ unit. This structure is 2.33 kJ mol⁻¹ higher in energy than the minimum C₃(I) structure. Thus, hydrogen scrambling via these two saddle point structures is quite facile. CH₅⁺ therefore, easily interconverts between its 120 equivalent minima, supporting the established fact that it is a highly fluxional molecule.

3.1.2. SiH₅⁺ and GeH₅⁺

The congeners of CH₅⁺, SiH₅⁺ and GeH₅⁺ were also optimized at MP2/aug-cc-pVTZ level. The optimized geometries of TH₅⁺ (T= Si and Ge) resemble a planar TH₃⁺ moiety complexed with an elongated H₂ unit. The C₃(I) structure has the H₂ unit eclipsed with the T-H bond (b) and is the minimum on the potential energy surface. The C₃(II) structure has the H₂ unit staggered with respect to the T-H bond (b). It is energetically quite close to the C₃(I) structure and is a first order saddle point having one imaginary frequency. This C₃(II) symmetry saddle point is the transition state via which rotation of the H₂ moiety about the TH₃⁺ frame occurs. However, in the case of SiH₅⁺ and GeH₅⁺ the C₃v structure is energetically higher than the dissociation energy of the complex and thus complete hydrogen scrambling is not facile [32,28].
The TH\(^{+}\) unit is nearly planar though the T-H bonds are not all equal. The tabulated bond distances (Tables 1 and 2) show that the T-H bonds in the TH\(^{+}\) molecule are slightly distorted from those computed for TH\(^{3+}\). Comparing the H-H bond distances for the H\(_2\) moiety in TH\(^{+}\) with the free H\(_2\) molecule, it seems that the H\(_2\) unit in TH\(^{+}\) is slightly elongated. The H-H distance in SiH\(^{+}\) is 0.7727Å and in GeH\(^{+}\) it is 0.7697Å, these are only slightly longer than the H-H distance in the free H\(_2\) molecule which is 0.7374Å. Therefore, the H\(_2\) moiety in TH\(^{+}\) seems to retain its identity in these molecules.

3.2. Atoms in Molecules (AIM) analysis

Bader’s ‘Atoms in Molecules’ (AIM) theory examines the topology of the electron density to understand the nature of bonding in molecules. The interaction between any two atoms is confirmed by the presence of a bond critical point (BCP) between them. The properties of the electron density at the BCP provide further insights about the bond. These topological properties for the TH\(^{+}\) (T= C, Si, and Ge) and C\(_2\)H\(_7^{+}\) are tabulated in Tables 3 and 4. The molecular graphs obtained from the AIM analysis are shown in Figures 4 and 5.

3.2.1. CH\(^{5+}\)

The molecular graphs for the three lowest lying stationary structures of CH\(^{5+}\) are shown in Figure 4. The C\(_s(\text{I})\) symmetry minimum structure is characterized by the presence of the five bond critical points (BCPs) which connect each of the H atoms to the C center. The value of the electron density (\(\rho\)) at the five BCPs ranges from 0.2174 to 0.2911 au and the Laplacian of electron density (\(\nabla^2 \rho\)) from -0.5017 to -1.2082 au. When \(\nabla^2 \phi\) at the BCP is negative and the \(\phi\) is large in magnitude, these interactions are referred to as shared interactions, which is characteristic of a covalent bond. Therefore, CH\(^{5+}\) is pentacoordinated with five covalent C-H bonds. The most striking observation however, is the absence of a bond critical point between the H atoms of the H\(_2\) moiety. The two long C-H bonds that make up the H\(_2\) moiety have very high ellipticity values (2.1739 and 1.3412) which suggests that these bonds are unstable. It is quite evident that CH\(^{5+}\) cannot be considered as a weakly bound complex of CH\(^{3+}\) and H\(_2\). These results agree with those obtained previously by Okulik et al. using the 6-311++G** basis set[10].

![Molecular graphs for the three lowest energy stationary structures of CH\(^{5+}\)calculated at MP2/aug-cc-PVTZ](image)

**Figure 4.** Molecular graphs for the three lowest energy stationary structures of CH\(^{5+}\)calculated at MP2/aug-cc-PVTZ
3.2.2. SiH$_5^+$ and GeH$_5^+$

The molecular graphs for SiH$_5^+$ and GeH$_5^+$ are quite different from that of CH$_5^+$ (Figure 5). It is evident that the slightly elongated H$_2$ moiety retains its identity. A bond critical point (BCP) is present between the two H atoms. The large magnitude of $\rho$ and the negative sign of $\nabla^2 \rho$ at the BCP (Table 4) indicate that a covalent bond is present between the two H atoms. The $\rho$ value in GeH$_5^+$ is larger than in SiH$_5^+$ which corroborates well with the computed H$_2$ bond lengths (Table 4).

The other prominent difference is the interaction between the planar cation and the H$_2$ moiety. The molecular graphs for SiH$_5^+$ and GeH$_5^+$ are best described as conflict structures. This is because the bond critical point between the two moieties connects the central T atom not with another atom but with the BCP between the two H atoms. This could be viewed as a bond between the $\sigma$ bond electrons of H$_2$ and the positive central T atom. Low values of $\rho$ at BCP and $\nabla^2 \rho$ at BCP being positive indicates a closed-shell interaction. Such an interaction is usually found in ionic bonds, hydrogen bonds, and van der Waals molecules.

The BCPs and bond paths clearly indicate the presence of the silyl/germyl cation interacting with an H$_2$ moiety. This interaction is indicative of a tetrel bonded interaction. The $\rho$ value for SiH$_5^+(0.0465$ au) and GeH$_5^+(0.0527$ au) is slightly higher than Koch and Popelier’s criterion for a C-H…O hydrogen bond [33] (0.002-0.034 au). Clearly, the tetrel bond in these cations are stronger than the strongest C-H…O hydrogen bond discussed in Koch and Popelier’s work. The Laplacian on the other hand for SiH$_5^+$ and GeH$_5^+$ is 0.1194 and 0.1267 respectively. These values are within the range for the criterion proposed by Koch and Popelier (0.024-0.139). Sosa and coworkers have suggested that the $|\lambda_1|/\lambda_3$
ratio must be less than 1 for a closed-shell interaction [34]. This ratio for SiH$_5^+$ and GeH$_5^+$ satisfy this criterion. The ellipticity values for these BCPs are quite large which is indicative of an unstable bond between these two units.

Table 3. Properties of the electron density at the BCP between the central atom and the H$_2$ moiety

| system  | ρ (au) | $\nabla^2 \rho$ (au) | ellipticity | $|\lambda_1|/\lambda_3$ |
|---------|--------|---------------------|-------------|---------------------|
| CH$_5^+$ | 0.2174 | -0.5017             | 2.1739      | 2.4190              |
|         | 0.2229 | -0.5586             | 1.3412      | 2.5094              |
| SiH$_5^+$ | 0.0465 | +0.1194             | 0.3878      | 0.2255              |
| GeH$_5^+$ | 0.0527 | +0.1267             | 0.3907      | 0.2643              |
| C$_2$H$_7^+$ | 0.2156 | -0.4653             | 32.2703     | 9.1543              |

Table 4. Properties of the electron density at the BCP between the H$_2$ moiety

| system  | ρ (au) | $\nabla^2 \rho$ (au) | ellipticity | $|\lambda_1|/\lambda_3$ |
|---------|--------|---------------------|-------------|---------------------|
| SiH$_5^+$ | 0.2506 | -1.0639             | 0.0753      | 1.4918              |
| GeH$_5^+$ | 0.2517 | -1.0745             | 0.0627      | 1.4722              |
| C$_2$H$_7^+$ | 0.2159 | -0.5173             | 6.7925      | 5.5024              |

Would the cations of larger alkane reveal a tetrel bond? In order to address this question, AIM analysis for C$_2$H$_7^+$ was carried out. The result is shown in Figure 6. There is a BCP between the two H atoms in C$_2$H$_7^+$, though the bond path is curved. This BCP appears very close to another BCP, connecting the H$_2$ to the C atom. A look at the bond ellipticity value at both these BCPs indicates that they are highly unstable (32.27 and 6.79) and therefore the molecular graph for this structure is highly unstable. In any case, this result indicates that there could be a tetrel bond between C and H$_2$ in favorable cases.

![Figure 6. Molecular graph for C$_2$H$_7^+$](image)

3.3. Natural Bond Orbital (NBO) Analysis

TH$_5^+$ (T= C, Si, and Ge) shows the presence of a 3c-2e H-T-H bond in the Natural Bond Orbital (NBO) analysis. In combination with the molecular graphs obtained from the AIM analysis, the 3c-2e bond in the case of CH$_5^+$ can be considered to be ‘open’ or ‘V’ type since there is no interaction between the
two H atoms. Whereas in the case of SiH₅⁺ and GeH₅⁺ we can consider it to be a ‘closed’ or ‘T’ type 3c-2e interaction since there is an H-H bond. A look at the nature of the orbitals reveals that the long C-H bonds in CH⁺ use sp³ orbitals from C and the equivalent bonds in SiH⁺ and GeH⁺ use an empty p orbital from the central atom which interacts with the H₂ unit. The charge analyses in both AIM and NBO reveal some interesting observations. The charge on the C atom in CH⁺ is negative and the H atoms carry the positive charge. This therefore reinforces the idea that CH⁺ is more like protonated methane than a CH⁺⋯H₂ complex. The charge analysis for SiH⁺ and GeH⁺ on the other hand reveals that the central T atom is positively charged and the two hydrogen atoms are negatively charged, indicating that it is TH⁺ and H₂.

3.4. Vibrational frequency analysis

Both AIM and NBO analyses do not give any evidence for the H---H bond in CH⁺ and both do give evidence for the same in TH⁺ (T= Si and Ge). Would the normal mode analysis on these three cations provide additional evidence about the bonding? Clearly TH⁺ has been considered as a weakly bound complex, with the central T atom tetrel bonded to the H₂ moiety. The positively charged central T atom can therefore accept electron density from the σ electrons of the H₂ moiety. This donation of electron density should lead to the weakening of the H₂ bond. The electron density (ρ) obtained from the AIM analysis shows that the H₂ bond is weakened more for SiH⁺ than for GeH⁺. An elongation of the H₂ bond length is expected as a consequence of the donation of electron density to the T center. The tabulated bond lengths show that the H₂ bond lengths in TH⁺ are elongated compared to free H₂. The H₂ bond in SiH⁺ is longer than in GeH⁺, this corroborates well with the computed electron density. It is evident that the H₂ unit retains its identity in the molecule. We therefore expect to find a normal mode in TH⁺ which comprises of the H₂ stretch. We then anticipate that the weakening and elongation of the bond would cause this H₂ stretch frequency to be red shifted. The computed harmonic frequencies are tabulated in Table 5. The H₂ stretch is red shifted by 466.65 cm⁻¹ in SiH⁺ and by 440.23 cm⁻¹ in GeH⁺. Boo and Lee obtained the infrared spectrum of the H—H stretching mode in SiH⁺ from 3650-3740 cm⁻¹, [25] reasonably close to the predicted value of 3800 cm⁻¹. In contrast there is no normal mode in CH⁺ which can be classified as H₂ stretch. There are two normal modes which involve the two H atoms and the central C atom. These are a symmetric and an antisymmetric stretch for the H-C-H unit. This provides further evidence that CH⁺ has two long and equivalent bonds but it is not a weak complex between CH⁺ and H₂.

Table 5. Harmonic frequencies of the H-H stretch calculated at MP2/ aug-cc-pVTZ and at B3LYP, also the scaled frequencies are reported. All values in cm⁻¹.

<table>
<thead>
<tr>
<th></th>
<th>MP2/ aug-cc-pVTZ</th>
<th>Scaled⁰</th>
<th>B3LYP /aug-cc-pVTZ</th>
<th>Scaledᵇ</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH⁺</td>
<td>No normal mode comprising of a H-H stretch</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiH⁺</td>
<td>4026.4</td>
<td>3825.1</td>
<td>3940.4</td>
<td>3820.5</td>
<td>3650-3740 [25]</td>
</tr>
<tr>
<td>GeH⁺</td>
<td>4054.2</td>
<td>3851.5</td>
<td>4006.9</td>
<td>3866.7</td>
<td>-</td>
</tr>
<tr>
<td>H₂</td>
<td>4517.6</td>
<td>4291.8</td>
<td>4417.7</td>
<td>4315.2</td>
<td>4401.21 [35]</td>
</tr>
</tbody>
</table>

⁰s scaling factor is 0.95
ᵇ scaling factor is 0.965
3.5. Potential Energy Scans

As discussed earlier, CH$_5^+$ is commonly considered protonated methane and H$_4$C$\cdots$HX complex could be thought of as the hydrogen bonded complex leading to it. However, the structure at the global minimum shows similarities with a weakly bound complex between CH$_5^+$ and H$_2$. All the results presented above clearly indicate that CH$_5^+$ neither has a tetrel bond or a bond between the two H atoms which are at a longer distance from C compared to the other three H atoms. Would the reaction path between CH$_5^+$ and CH$_3^+$ + H$_2$ indicate the presence of a tetrel bond anywhere along the reaction coordinate? To address this question, the potential energy scan was done at MP2/aug-cc-pVDZ level by varying the distance between the TH$_3^+$ unit and the H$_2$ moiety. The AIM analysis was carried out at various points along the reaction coordinate. The results for CH$_5^+$ are shown in Figure 7 and the results for SiH$_5^+$ and GeH$_5^+$ are shown in the Supporting Information.

In all these cases the AIM analysis indicates that there is no tetrel bond formation between H$_2$ and TH$_3^+$ as the H$_2$ approaches TH$_3^+$ until very close to the minimum. In the CH$_5^+$ case the tetrel bond is not found anywhere along this coordinate and for SiH$_5^+$ and GeH$_5^+$, only at the minimum a tetrel bond is seen. In all cases one of the hydrogen atoms is interacting with the central atom along the reaction coordinate and this interaction is likely the driving force for the reaction. There is a bond path connecting one hydrogen atom to the central atom which may be considered as a tetrel bond.

![Figure 7. Potential energy scan for changing the distance between the CH$_5^+$ and H$_2$ moieties](image-url)
4. Discussions

The C₁₅(I) symmetry is the global minimum structure for TH₅⁺. The H₂ moiety retains its identity in SiH₅⁺ and GeH₅⁺ though the H₂ bond is slightly elongated. In the case of CH₅⁺ the H₂ moiety is elongated to such an extent that it can no longer be considered as a separate unit. The two long C-H bonds that make up the H₂ moiety are similar to the other C-H bonds of the CH₃⁺ tripod and the AIM parameters at all their BCPs clearly show that all five C-H bonds are covalent, though two of them are slightly weaker than the other three.

The AIM analysis clearly shows that the CH₅⁺ has five covalent C-H bonds and the TH₅⁺(T = Si/Ge) molecules are a weakly bound complex of the TH⁺ cation and H₂. The SiH₅⁺ and GeH₅⁺ are bound by a tetrel bond. The NBO analysis shows that all the TH₅⁺ molecules have a 3c-2e bond and the AIM analysis points out significant differences between CH₅⁺ and SiH₅⁺/GeH₅⁺. We propose that the 3c-2e bonds in conjunction with the molecular graph obtained from the AIM analysis can be classified as a ‘V’ or ‘T’ type 3c-2e bond. Naturally, some questions arise. Is there any molecular system having a 3c-2e bonds in which every atom is connected by a bond to the other two atoms, such as ‘Δ’? Or is there a system where the three atoms are arranged linearly with the central atom bonded to the other two atoms? Though 3c-2e bonds have been discussed extensively [36–38] and it is a text-book material, we could not find such clear classifications anywhere.

![Molecular Graphs](image)

**Figure 8.** The molecular graphs showing different types of 3c-2e bonds.
For the sake of completeness, AIM analysis was carried out on well known examples such as C3H3+ and H3+, which are expected to be Δ-type 3c-2e bonds. The results are shown in Figure 8. The C3H3+ does show a Δ-type 3c-2e bond and H3+ is different from all the cases discussed so far and the molecular graph looks like Y. Interestingly as shown in the previous section C3H3+ shows a Y type 3c-2e bond. Jensen had drawn a Y type bond for CH5+[37], based on intuition, unlike the V type bond that has been observed in this work and also in the previous AIM analysis by Okulik et al. Jemmis, Chandrashekar and Schleyer have investigated linear 3c-2e bonds in CH3Li2+ and other similar CH3M2+ systems, pointing out the role these structures play in the stereochemistry of the S2 reactions [39]. Clearly, describing the bonding in any molecular system as 3c-2e bond does not reveal much about how the three centres are bonded. The 3c-2e bonds could be V-type, T-type, Δ-type, Y-type or linear. A more detailed description of 3c-2e bond is beyond the scope of this work and clearly would be a digression on the main focus of this work i.e. structure and bonding in TH5+.

The harmonic frequencies for the TH5+ molecules show that the H2 moiety retains its identity in SiH5+ and GeH5+. The H2 stretching frequency in these molecules is red shifted from the free H2 frequency because of the elongation in the H2 bond. CH5+ is distinctly different with no pure H2 vibration. C3H5+ which is the higher homologue of CH5+ has an H-H interaction as evident from its molecular graph, but the frequency analysis shows that there is no normal mode which corresponds to a pure H-H stretch. This indicates that the normal modes of the Y-type 3c-2e bonds could be different from those of the T-type. Therefore, though it seems by examining the molecular graphs that only CH5+ is different from its congeners and its homologues, the frequency analysis provides evidence that the carbocations (CH5+ and C3H5+) are different from their congeners (SiH5+ and GeH5+).

Why is the structure of CH5+ distinctly different from that of its congeners, SiH5+ and GeH5+? This question can be answered by analyzing all the bond energies involved as well as the dissociation energies for the TH5+ molecules. The relevant bond energies are given in Tables 6 and 7. If we consider the formation of the CH5+ molecule to be the hydrogenation of the CH3+ species, it is evident that two C-H bonds are formed at the expense of one H-H bond. The C-H and H-H bond energies are nearly equal and the two weak C-H bonds can be easily formed by cleaving the H-H bond in H2. This arrangement is more stable than having a slightly weaker H-H bond and a tetrel bond with the C atom in CH3+. This is not the case with SiH5+ and GeH5+, as the Si-H and Ge-H bonds are significantly weaker than H-H bond. The formation of two weak T-H bonds cannot compensate for the cleavage of the H-H bond and therefore SiH5+ and GeH5+ prefer to form a tetrel bonded complex of the TH3+ species with H2. In general, Si and Ge form a stronger tetrel bond than C [18]. The combination of the tetrel bond and H-H bond is energetically more preferred than having two weak T-H bonds, when T = Si/Ge. The difference between the structures of CH5+ and SiH5+ has been rationalized on the basis of their bond energies by Schleyer et al.[24]. Our analysis includes the bond energies of the T-H bonds and that of the tetrel bond between T+ and H2, vide infra.

The proton affinities of TH4 are given in Table 6 as well. At first look, it appears counterintuitive to find the order CH4< SiH4< GeH4 given the reverse order for the T-H bond energy. The proton affinity of CH4 is about 100 kJ mol⁻¹ less than that of SiH4, which is about 40 kJ mol⁻¹ less than that of GeH4. This in a way provides further evidence to the structure of TH5+. While the protonation of CH4 results in the formation of two relatively weaker C-H bonds, protonation of SiH4 and GeH4 results in the formation of H-H bond and a tetrel bond.
The dissociation energies calculated for the TH⁺⁺⁺⁺ molecules going to TH⁺⁺ and H₂ are given in Table 7. The CH⁺⁺ requires the most energy (~182.99 kJ mol⁻¹) to dissociate into a methyl cation and H₂. It is higher by nearly 133 kJ mol⁻¹ when compared with SiH⁺⁺⁺⁺. However, this is not the ‘tetrel bond energy’ between CH⁺⁺ and H₂ as it does not exist in CH⁺⁺⁺⁺. This high energy is due to the fact that the two C–H bonds need to be broken before forming the H–H bond. The SiH⁺⁺⁺⁺ and GeH⁺⁺⁺⁺ have nearly equal dissociation energies (49.7 and 43.8 kJ mol⁻¹, respectively) and these can be readily identified as the tetrel bond energy. These values are larger than the typical tetrel bond energies for neutral molecules, typically less than 16 kJ mol⁻¹ [17,18]. Our results are compared with previous calculated and experimental values in Table 7 and the trends are similar.

Table 6. T-H bond energies and proton affinities for the TH⁺⁺⁺⁺ molecule in kJ mol⁻¹.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond Energy (kJ mol⁻¹) [40]</th>
<th>Molecule</th>
<th>Proton Affinity (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C–H</td>
<td>423</td>
<td>CH⁺⁺⁺⁺</td>
<td>-546.01 ± 8.4 [41]</td>
</tr>
<tr>
<td>Si–H</td>
<td>398.3</td>
<td>SiH⁺⁺⁺⁺</td>
<td>-640.15 ± 12.6 [42]</td>
</tr>
<tr>
<td>Ge–H</td>
<td>365</td>
<td>GeH⁺⁺⁺⁺</td>
<td>-682.15 ± 3.9 [26]</td>
</tr>
<tr>
<td>H–H</td>
<td>432</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 7. Hydrogenation energies for the TH⁺⁺⁺⁺ molecules.

<table>
<thead>
<tr>
<th>TH⁺⁺⁺⁺ + H₂ → TH⁺⁺⁺⁺</th>
<th>Calculated hydrogenation energy (kJ mol⁻¹)</th>
<th>Experimental hydrogenation energyb</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>This worka</td>
<td>Previous results</td>
</tr>
<tr>
<td>CH⁺⁺⁺⁺ + H₂ → CH⁺⁺⁺⁺</td>
<td>-183.0</td>
<td>-141.8[24]</td>
</tr>
<tr>
<td>SiH⁺⁺⁺⁺ + H₂ → SiH⁺⁺⁺⁺</td>
<td>-49.7</td>
<td>-30.1[24]</td>
</tr>
<tr>
<td>GeH⁺⁺⁺⁺ + H₂ → GeH⁺⁺⁺⁺</td>
<td>-43.8</td>
<td>-31.8[27]</td>
</tr>
</tbody>
</table>

a calculated at MP2/aug-cc-pVTZb Reference [24] and references therein

5. Conclusions

The structures of TH⁺⁺⁺⁺ (T = C/Si/Ge) have been analyzed based on AIM, NBO and normal coordinate analysis. All these results give a consistent picture. The CH⁺⁺⁺⁺ has a pentacoordinate carbon, having three shorter C–H bonds and two longer C–H bonds. Both SiH⁺⁺⁺⁺ and GeH⁺⁺⁺⁺ have a structure in which the ‘TH⁺⁺⁺⁺’ is tetrel bonded to H₂. Bond energies, proton affinities and hydrogenation energies are all consistent with these structures. We conclude that the common description of CH⁺⁺⁺⁺ as a complex between CH⁺⁺ and H₂ is not consistent with all the results presented here. Thus, CH⁺⁺⁺⁺ has no hydrogen bond or carbon bond, and SiH⁺⁺⁺⁺ and GeH⁺⁺⁺⁺ have a tetrel bond.

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References


30. Keith, T. A. AIMAll (Version 16.05.18),TK Gristmill Software. *Overland Park KS USA (aim.tkgristmill.com)* **2016**.


