Inter/intramolecular Bonds in TH_5^+ (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 TH_5^+ (T = C/Si/Ge). All these analyses lead to a consistent structure for these three protonated TH_4 molecules. The CH_5^+ 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 CH_3^+ and H_2 is inconsistent with these results. However, SiH_5^+ and GeH_5^+ are both indeed a complex formed between TH_3^+ and H_2 stabilized by a tetrel bond, with the H_2 being the tetrel bond acceptor. The three-center-two-electron bond (3c-2e) in CH_5^+ has an open structure, which can be characterized as a V-type 3c-2e bond and that found in SiH_5^+ and GeH_5^+ 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 TH_5^+ can explain the trend in proton affinity of TH_4. 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_3O^+) and ammonium ion (NH_4^+) are formed by the protonation of H_2O and NH_3, respectively. These are often mediated by a hydrogen bonded complex such as $H_2O\cdots HX$ or $H_3N\cdots HX$. Rotational spectroscopic investigations on several $CH_4\cdots HX$ (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_3O^+ 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^+?
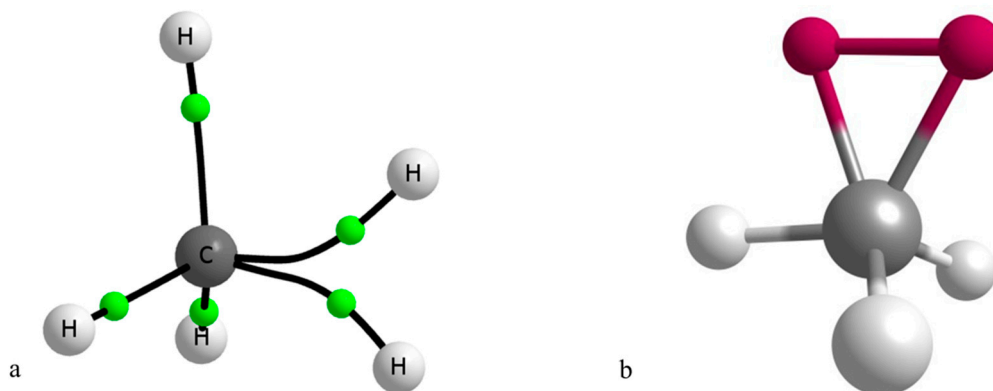
Figure 1.(a) Molecular graph for CH_5^+; (b) CH_5^+as depicted in Reference 19.

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].

GeH$_5^+$ 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 GeH$_5^+$ to be a loose complex between the germyl cation (GeH$_3^+$) and H$_2$ [27]. The comprehensive study of all the structures of the GeH$_5^+$ by Schreiner et al. concluded that the geometry having C$_s$ symmetry was the minimum on the potential energy surface [28]. It is evident that the ground state minimum structure for the TH$_5^+$ molecule has C$_s$ symmetry.

Theoretical and spectroscopic results for SiH$_5^+$ and GeH$_5^+$ suggest that these are weakly bound complexes of the TH$_3^+$ (T= Si, and Ge) cation with H$_2$. The topological analysis of the charge density would then allow us to observe a tetrel bonded interaction between the TH$_3^+$ cation and the H$_2$ 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 SiH$_5^+$ and GeH$_5^+$ with CH$_5^+$ 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 CH$_5^+$. The results are presented here.

2. Computational methods

The geometries of the TH$_5^+$ 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 TH$_3^+$ moiety and H$_2$. 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 TH$_5^+$ 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 TH$_5^+$ 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 TH$_5^+$ species were analyzed using NBO6.0 as implemented in Gaussian 09 [31].

3. Results

3.1. Optimized geometries

3.1.1 CH$_5^+$

Methane distorts to accommodate the presence of the added proton to form CH$_5^+$. The CH$_5^+$ molecule was optimized at MP2/ aug-cc-pVTZ. The three lowest energy stationary structures obtained are shown below in Figure 2. The geometry with C$_s$(I) symmetry is a minimum on the potential energy surface which is confirmed by the vibrational frequency analysis. The CH$_3$ 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.

C_s (I)
$E_{rel} = 0$ kJmol^{-1}
[0]

C_s (II)
$E_{rel} = 0.59$ kJmol^{-1}
[1]

C_{2v}
$E_{rel} = 2.33$ kJmol^{-1}
[1]
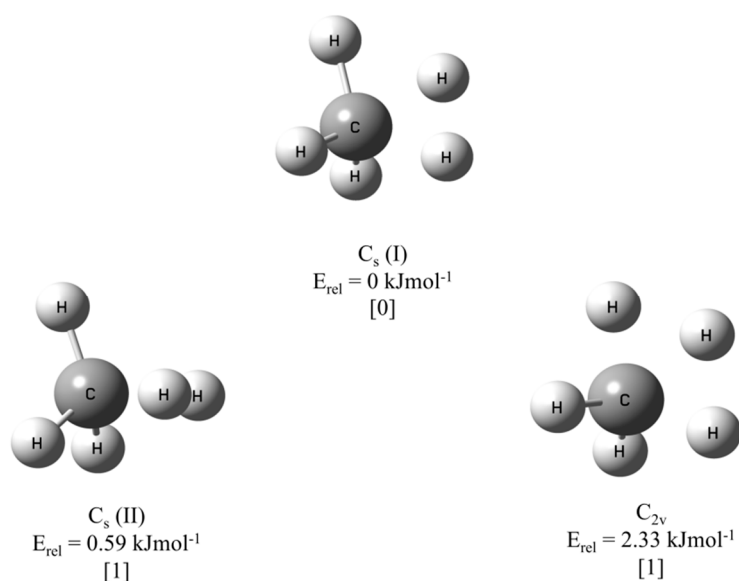
Figure 2. Optimized geometries and relative energies of three lowest energy stationary structures of CH_5^+ calculated at MP2/aug-cc-pVTZ. Number in brackets denotes number of imaginary frequencies.

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 0.1Å 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_s (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.
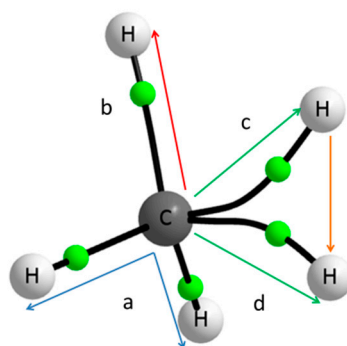
Figure 3. The different T-H bonds in TH_5^+

Table 1. Bond lengths calculated at MP2/aug-cc-pVTZ

MP2/aug-cc-pVTZ	a(Å)	b(Å)	c(Å)	d(Å)	H-H (Å)
CH_5^+	1.0852 1.0852	1.1072	1.1835	1.1819	0.9748
SiH_5^+	1.4606 1.4605	1.4626	1.8790	1.8842	0.7727
GeH_5^+	1.4985 1.4985	1.5002	1.9477	1.9532	0.7697

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

Molecule	T-H (Å)	Molecule	T-H (Å)	Molecule	H-H (Å)
CH_4	1.0863	CH_3^+	1.0867		
SiH_4	1.4788	SiH_3^+	1.4618	H_2	0.7374
GeH_4	1.5118	GeH_3^+	1.5007		

The second stationary structure is a saddle point on the potential energy surface, confirmed by the presence of an imaginary frequency. This structure has C_s (II) symmetry with the H_2 moiety staggered with respect to the unique C-H bond (b). The C_s (II) saddle point is the transition state for the rotation of the H_2 unit about the pseudo C_3 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 C_s(I) structure. Therefore, the rotation of the H_2 moiety about the pseudo C_3 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 C_{2v} symmetry structure is the transition state on the reaction coordinate where the H atom flips between the H_2 moiety and the CH_3 unit. This structure is 2.33 kJ mol^{-1} higher in energy than the minimum C_s(I) structure. Thus, hydrogen scrambling via these two saddle point structures is quite facile. CH_5^+ therefore, easily interconverts between its 120 equivalent minima, supporting the established fact that it is a highly fluxional molecule.

3.1.2. SiH_5^+ and GeH_5^+

The congeners of CH_5^+, SiH_5^+ and GeH_5^+ were also optimized at MP2/aug-cc-pVTZ level. The optimized geometries of TH_5^+ (T= Si and Ge) resemble a planar TH_3^+ moiety complexed with an elongated H_2 unit. The C_s (I) structure has the H_2 unit eclipsed with the T-H bond (b) and is the minimum on the potential energy surface. The C_s (II) structure has the H_2 unit staggered with respect to the T-H bond (b). It is energetically quite close to the C_s (I) structure and is a first order saddle point having one imaginary frequency. This C_s (II) symmetry saddle point is the transition state via which rotation of the H_2 moiety about the TH_3^+ frame occurs. However, in the case of SiH_5^+ and GeH_5^+ the C_{2v} structure is energetically higher than the dissociation energy of the complex and thus complete hydrogen scrambling is not facile [32,28].

The TH_3^+ 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_5^+ molecule are slightly distorted from those computed for TH_3^+. Comparing the H-H bond distances for the H_2 moiety in TH_5^+ with the free H_2 molecule, it seems that the H_2 unit in TH_5^+ is slightly elongated. The H-H distance in SiH_5^+ is 0.7727Å and in GeH_5^+ 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_5^+ 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_5^+ (T= C, Si, and Ge) and $C_2H_7^+$ 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(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 (ϱ) at the five BCPs ranges from 0.2174 to 0.2911 au and the Laplacian of electron density ($\nabla^2\varrho$) from -0.5017 to -1.2082 au. When $\nabla^2\varrho$ at the BCP is negative and the ϱ 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].
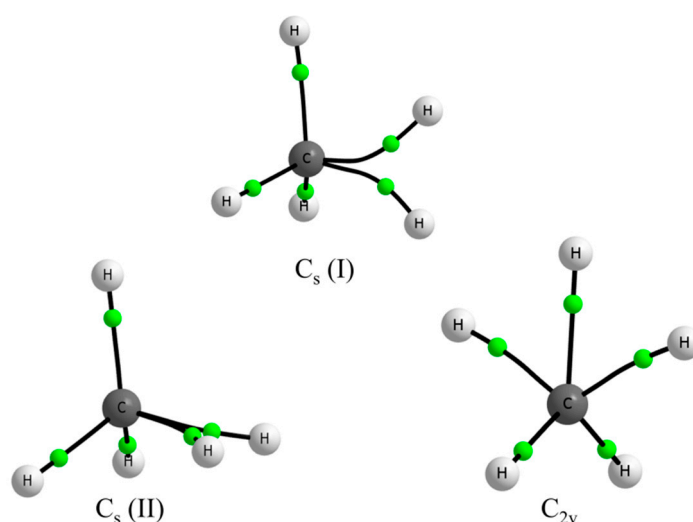
Figure 4. Molecular graphs for the three lowest energy stationary structures of CH_5^+ calculated at MP2/aug-cc-PVTZ
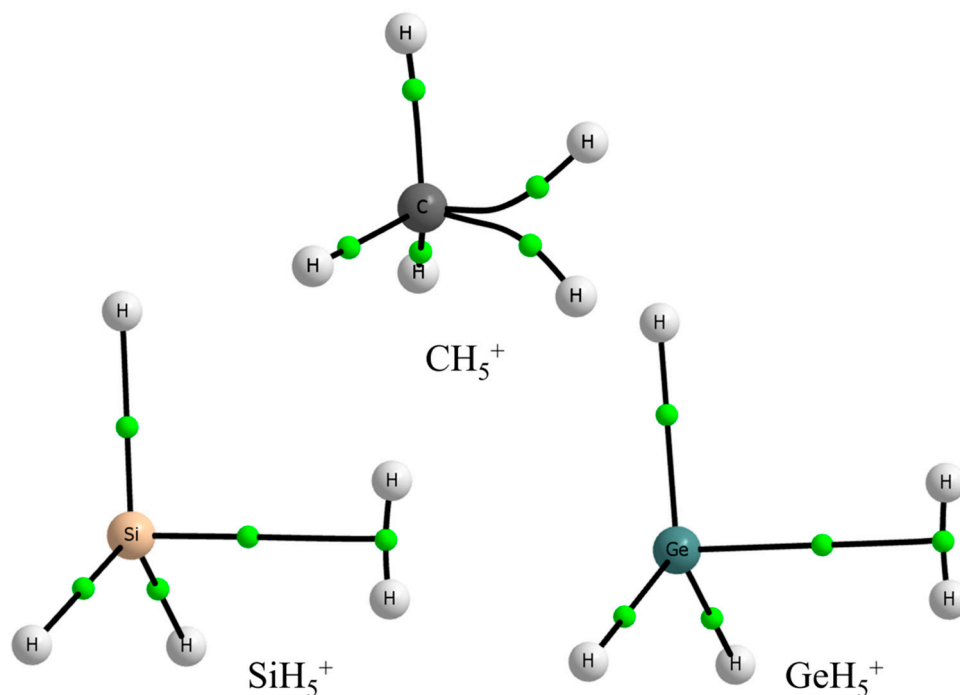
Figure 5. Molecular graphs for the TH_5^+ molecule calculated at MP2/aug-cc-pVTZ

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 ϱ and the negative sign of $\nabla^2\varrho$ at the BCP (Table 4) indicate that a covalent bond is present between the two H atoms. The ϱ 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 σ bond electrons of H_2 and the positive central T atom. Low values of ϱ at BCP and $\nabla^2\varrho$ 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 ϱ 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	$\varrho(au)$	$\nabla^2\varrho(au)$	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
$C_2H_7^+$	0.2156	-0.4653	32.2703	9.1543

Table 4. Properties of the electron density at the BCP between the H_2 moiety

system	$\varrho(au)$	$\nabla^2\varrho(au)$	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
$C_2H_7^+$	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 $C_2H_7^+$ was carried out. The result is shown in Figure 6. There is a BCP between the two H atoms in $C_2H_7^+$, 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.
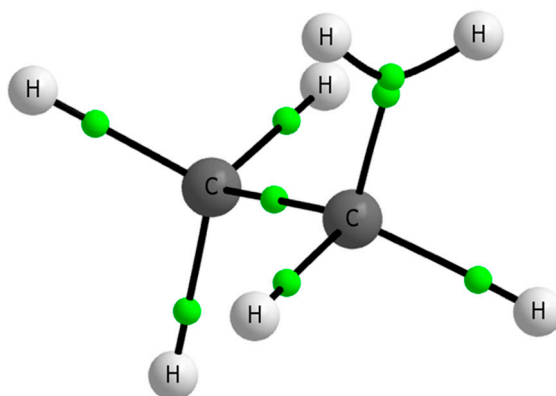
Figure 6. Molecular graph for $C_2H_7^+$

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 SiH_5^+ and GeH_5^+ 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_5^+ use sp^3 orbitals from C and the equivalent bonds in SiH_5^+ and GeH_5^+ use an empty p orbital from the central atom which interacts with the H_2 unit. The charge analyses in both AIM and NBO reveal some interesting observations. The charge on the C atom in CH_5^+ is negative and the H atoms carry the positive charge. This therefore reinforces the idea that CH_5^+ is more like protonated methane than a $CH_3^+ \cdots H_2$ complex. The charge analysis for SiH_5^+ and GeH_5^+ 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_3^+ and H_2.

3.4. Vibrational frequency analysis

Both AIM and NBO analyses do not give any evidence for the H---H bond in CH_5^+ and both do give evidence for the same in TH_5^+ (T= Si and Ge). Would the normal mode analysis on these three cations provide additional evidence about the bonding? Clearly TH_5^+ has been considered as a weakly bound complex, with the central T atom tetrel bonded to the H_2 moiety. The positively charged central T atom can therefore accept electron density from the σ electrons of the H_2 moiety. This donation of electron density should lead to the weakening of the H_2 bond. The electron density (ϱ) obtained from the AIM analysis shows that the H_2 bond is weakened more for SiH_5^+ than for GeH_5^+. An elongation of the H_2 bond length is expected as a consequence of the donation of electron density to the T center. The tabulated bond lengths show that the H_2 bond lengths in TH_5^+ are elongated compared to free H_2. The H_2 bond in SiH_5^+ is longer than in GeH_5^+, this corroborates well with the computed electron density. It is evident that the H_2 unit retains its identity in the molecule. We therefore expect to find a normal mode in TH_5^+ which comprises of the H_2 stretch. We then anticipate that the weakening and elongation of the bond would cause this H_2 stretch frequency to be red shifted. The computed harmonic frequencies are tabulated in Table 5. The H_2 stretch is red shifted by 466.65 cm^{-1} in SiH_5^+ and by 440.23 cm^{-1} in GeH_5^+. Boo and Lee obtained the infrared spectrum of the H–H stretching mode in SiH_5^+ 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_5^+ which can be classified as H_2 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_5^+ has two long and equivalent bonds but it is not a weak complex between CH_3^+ and H_2.

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}.

|	MP2/ aug-cc-pVTZ	Scaled[a]	B3LYP /aug-cc-pVTZ	Scaled[b]	Experimental
CH_5^+	No normal mode comprising of a H-H stretch				
SiH_5^+	4026.4	3825.1	3940.4	3802.5	3650-3740 [25]
GeH_5^+	4054.2	3851.5	4006.9	3866.7	-
H_2	4517.6	4291.8	4417.7	4315.2	4401.21 [35]

[a]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 $H_4C\cdots HX$ 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_3^+ 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.
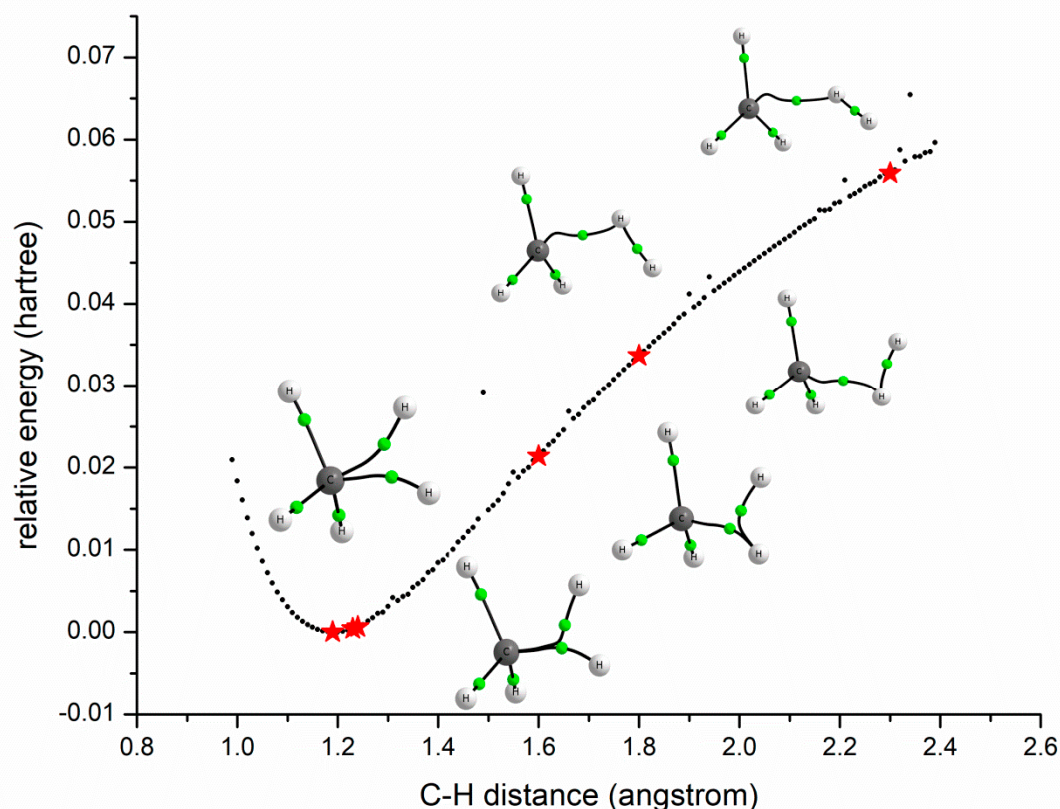

Figure 7. Potential energy scan for changing the distance between the CH_3^+ and H_2 moieties

4. Discussions

The C_s (I) symmetry is the global minimum structure for TH_5^+. The H_2 moiety retains its identity in SiH_5^+ and GeH_5^+ though the H_2 bond is slightly elongated. In the case of CH_5^+ the H_2 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 H_2 moiety are similar to the other C-H bonds of the CH_3^+ 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 CH_5^+ has five covalent C-H bonds and the TH_5^+(T = Si/Ge) molecules are a weakly bound complex of the TH_3^+ cation and H_2. The SiH_5^+ and GeH_5^+ are bound by a tetrel bond. The NBO analysis shows that all the TH_5^+ molecules have a 3c-2e bond and the AIM analysis points out significant differences between CH_5^+ and SiH_5^+/GeH_5^+. 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.
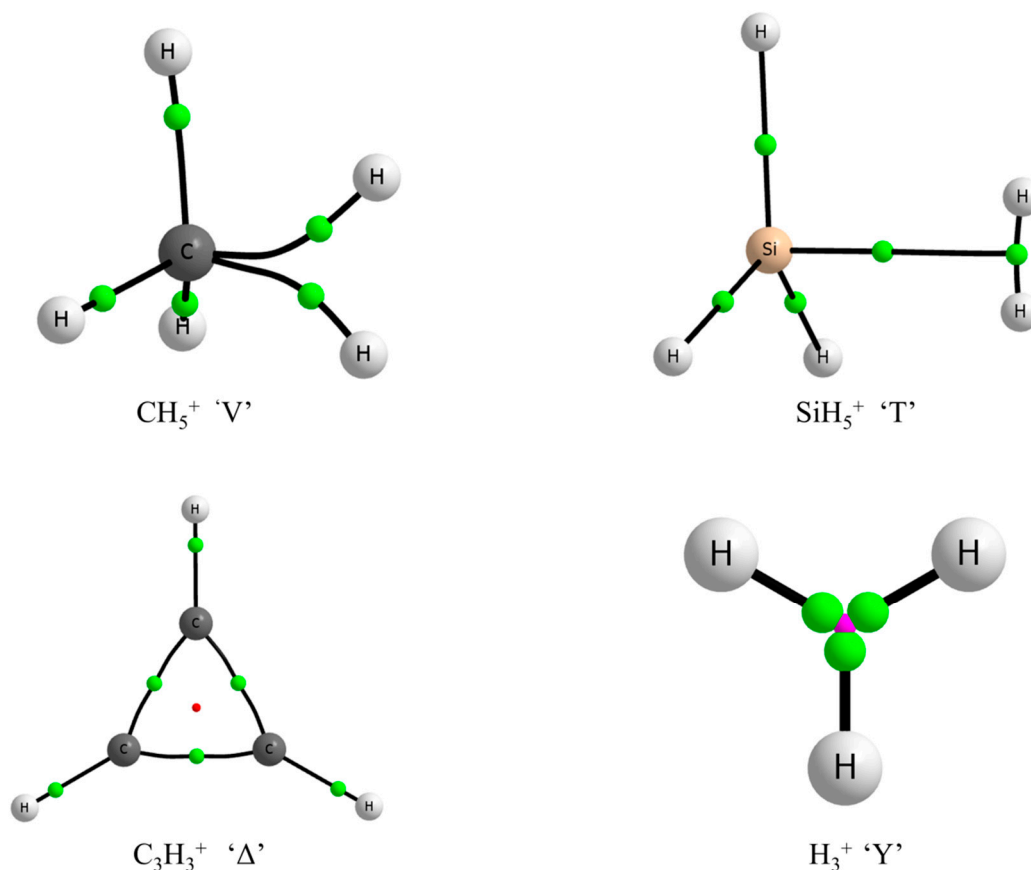
Figure 8. The molecular graphs showing different types of 3c-2e bonds.

For the sake of completeness, AIM analysis was carried out on well known examples such as $C_3H_3^+$ and H_3^+, which are expected to be Δ-type 3c-2e bonds. The results are shown in Figure 8. The $C_3H_3^+$ does show a Δ-type 3c-2e bond and H_3^+ is different from all the cases discussed so far and the molecular graph looks like Y. Interestingly as shown in the previous section $C_2H_7^+$ shows a Y type 3c-2e bond. Jensen had drawn a Y type bond for CH_5^+[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 $CH_3Li_2^+$ and other similar $CH_3M_2^+$ systems, pointing out the role these structures play in the stereochemistry of the S_E2 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 TH_5^+.

The harmonic frequencies for the TH_5^+ molecules show that the H_2 moiety retains its identity in SiH_5^+ and GeH_5^+. The H_2 stretching frequency in these molecules is red shifted from the free H_2 frequency because of the elongation in the H_2 bond. CH_5^+ is distinctly different with no pure H_2 vibration. $C_2H_7^+$ which is the higher homologue of CH_5^+ 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 CH_5^+ is different from its congeners and its homologues, the frequency analysis provides evidence that the carbocations (CH_5^+ and $C_2H_7^+$) are different from their congeners (SiH_5^+ and GeH_5^+).

Why is the structure of CH_5^+ distinctly different from that of its congeners, SiH_5^+ and GeH_5^+? This question can be answered by analyzing all the bond energies involved as well as the dissociation energies for the TH_5^+ molecules. The relevant bond energies are given in Tables 6 and 7. If we consider the formation of the CH_5^+ molecule to be the hydrogenation of the CH_3^+ 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 H_2. This arrangement is more stable than having a slightly weaker H-H bond and a tetrel bond with the C atom in CH_3^+. This is not the case with SiH_5^+ and GeH_5^+, 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 SiH_5^+ and GeH_5^+ prefer to form a tetrel bonded complex of the TH_3^+ species with H_2. 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 CH_5^+ and SiH_5^+ 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 H_2, vide infra.

The proton affinities of TH_4 are given in Table 6 as well. At first look, it appears counterintuitive to find the order $CH_4 < SiH_4 < GeH_4$ given the reverse order for the T-H bond energy. The proton affinity of CH_4 is about 100 kJ mol^{-1} less than that of SiH_4, which is about 40 kJ mol^{-1} less than that of GeH_4. This in a way provides further evidence to the structure of TH_5^+. While the protonation of CH_4 results in the formation of two relatively weaker C-H bonds, protonation of SiH_4 and GeH_4 results in the formation of H-H bond and a tetrel bond.

The dissociation energies calculated for the TH_5^+ molecules going to TH_3^+ and H_2 are given in Table 7. The CH_5^+ requires the most energy (-182.99 kJ mol^{-1}) to dissociate into a methyl cation and H_2. It is higher by nearly 133 kJ mol^{-1} when compared with SiH_5^+. However, this is not the 'tetrel bond energy' between CH_3^+ and H_2 as it does not exist in CH_5^+. 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_5^+ and GeH_5^+ have nearly equal dissociation energies (49.7 and 43.8 kJmol^{-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 kJmol^{-1} [17,18]. Our results are compared with previous calculated and experimental values in Table 7 and the trends are similar.

Table 6. T-HBond energies and proton affinities for the TH_4 molecule in kJmol^{-1}.

Bond	Bond Energy (kJmol^{-1}) [40]	Molecule	Proton Affinity (kJmol^{-1})
C-H	423	**CH$_4$**	-546.01 ± 8.4 [41]
Si-H	398.3	**SiH$_4$**	-640.15 ± 12.6 [42]
Ge-H	365	**GeH$_4$**	-682.15 ±3.9 [26]
H-H	432		

Table 7. Hydrogenation energies for the TH_3^+ molecules.

$TH_3^+ + H_2 \rightarrow TH_5^+$	Calculated hydrogenation energy (kJmol^{-1})		Experimental hydrogenation energy[b]
	This work[a]	Previous results	
CH$_3^+$ + H$_2$ → CH$_5^+$	-183.0	-141.8[24]	-175.7 ± 8.4
SiH$_3^+$ + H$_2$ → SiH$_5^+$	-49.7	-30.1[24]	-79.5 ± 12.5
GeH$_3^+$ + H$_2$ → GeH$_5^+$	-43.8	-31.8[27]	-

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

5. Conclusions

The structures of TH_5^+ (T = C/Si/Ge) have been analyzed based on AIM, NBO and normal coordinate analysis. All these results give a consistent picture. The CH_5^+ has a pentacoordinate carbon, having three shorter C-H bonds and two longer C-H bonds. Both SiH_5^+ and GeH_5^+ have a structure in which the TH_3^+ is tetrel bonded to H_2. Bond energies, proton affinities and hydrogenation energies are all consistent with these structures. We conclude that the common description of CH_5^+ as a complex between CH_3^+ and H_2 is not consistent with all the results presented here. Thus, CH_5^+ has no hydrogen bond or carbon bond, and SiH_5^+ and GeH_5^+ have a tetrel bond.

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