Symmetry breaking and structural distortions in charged $\text{XH}_4$ ( $\text{X} = \text{C}, \text{Si}, \text{Ge}, \text{Sn}$ and $\text{Pb}$ ) molecules

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Abstract

We have investigated the ground state structures of neutral and charged $\text{XH}_4$ ( $\text{X} = \text{C}, \text{Si}, \text{Ge}, \text{Sn}$ and $\text{Pb}$ ) molecules using the first-principles electronic structure methods. The structure of positively charged molecules for $\text{X} = \text{Si}, \text{Ge}, \text{Sn}$ and $\text{Pb}$ is characterized by a severe distortion from tetrahedral structure and an unusual H-H bond while the negatively charged molecules get distorted by pushing two hydrogen atoms away from each other. However, $\text{CH}_4^+$ and $\text{CH}_4^-$ are exceptions to this behavior. We provide an insight into the symmetry breaking mechanism and unusual H-H bonding using simple electrostatic arguments based on the unequal charge distribution on H atoms. Those charged molecules having unequal charge distribution on H atoms get distorted due to different electrostatic forces between the atoms. We show that the directionality and occupation of the highest occupied molecular orbital (HOMO) play an important role in creating charge asymmetry in these molecules.

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I. INTRODUCTION

Although neutral XH4 (X = C, Si, Ge, Sn and Pb) molecules have tetrahedral symmetry, charging these molecules breaks this symmetry. The symmetry breaking in general is associated with a large structural distortion and in many cases unusual H-H bonding arrangement. Some of these clusters have been investigated earlier and the symmetry breaking has been attributed to the Jahn-Teller effect. In the Jahn-Teller effect [1, 2, 3], electrons occupying a degenerate level favor a low symmetric structure by lifting the degeneracy. For example, the highest occupied molecular orbital (HOMO) of tetrahedral SiH4 is triply degenerate. When an electron is removed from SiH4, its structure gets distorted drastically due to the Jahn-Teller effect [4, 5, 6, 7, 8].

The structure of SiH4+ has been investigated by a large number of workers [4, 5, 6, 7, 8] and it took almost a decade to settle its ground state structure. Now it is generally agreed that the ground state structure of SiH4+ has Cs symmetry. Similarly, the structure of CH4+ has been studied extensively [8, 9, 10, 11, 12, 13, 14, 15, 16], though there is still ambiguity regarding its ground state structure. The calculations done by the density functional theory (DFT) methods show that the ground state structure of CH4+ has D2d symmetry [8, 9], while the Hartree-Fock (HF) and post HF calculations show the ground state structure as C2v [9, 16]. The lowering of tetrahedral symmetry of CH4+ and SiH4+ has been attributed to the Jahn-Teller effect. However, the structure of CH4+ is quite different from that of SiH4+. It is difficult to understand the difference between the CH4+ and SiH4+ distortions only from the Jahn-Teller effect. This is because the Jahn-Teller theorem only suggests the existence of distortion and says nothing regarding the nature and magnitude of the distortion.

In this paper we focus on the ground state structures of charged XH4 molecules using the first-principles electronic structure methods and provide an insight into the symmetry breaking mechanism. We find that upon charging most of the molecules undergo large structural distortion which can be attributed to the Jahn-Teller effect. Further, the nature of distortions of positively charged molecules is different from that of negatively charged molecules. Interestingly, most of the positively charged molecules have an unusual H-H bond and appear like transition states of unstable XH2+ and H2 complex. We try to understand the distortions, unusual H-H bonding and stability of these molecules. Vibrational analysis shows that these molecules are not transition states. The calculated fragmentation energy
indicates that the stability of XH₄⁺ molecules decreases from CH₄⁺ to PbH₄⁺.

Using various exchange-correlation functionals such as local density approximation (LDA), local spin density approximation (LSDA), gradient corrected approximation (GGA) and spin-polarized GGA (GGA-SP) we have investigated the effect of different occupations in charged tetrahedral XH₄ molecules. Our calculations show that the configuration corresponding to integer occupancy and asymmetrical charge density leads to the lowest energy. We provide simple arguments in terms of charge asymmetry and electrostatic interaction between atoms which explain the nature of distortions in charged XH₄ molecules. For example, we are able to explain why the nature of distortion of SiH₄⁺ differs from CH₄⁺ and why the positively charged molecules distort differently from the negatively charged molecules. We study the structural distortions of SiH₄⁺ in detail using conjugate gradient method and show that the evolution of the structure is governed by the electrostatic interaction between the atoms. Our investigations reveal that the distribution of charges on H atoms plays an important role in distorting the charged molecules. If the charges on H atoms are not equal, the structure gets distorted due to different electrostatic forces on the atoms. We also discuss how the charge asymmetry is created in these molecules by the directionality and occupation of the HOMO.

The plan of the paper is as follows. In section II we give computational details of the present work. Section III contains results and discussion and finally in section IV we give our conclusions.

II. COMPUTATIONAL DETAILS

We have investigated the structure of neutral and charged XH₄ using Vienna *ab-initio* simulation package (VASP)[17] and Gaussian98[18] package. We have cross checked our calculations using both packages and find that the results obtained by both methods are in good agreement. A number of calculations were done using the unrestricted Hartree-Fock (UHF) and DFT methods using the Gaussian98 package. In the DFT calculations we have used several exchange-correlation functionals such as Slater’s exchange with the local correlation functional of Perdew (SPL), Becke’s exchange which includes gradient density with gradient corrected correlation functional (BPW91) and Becke’s 3 parameter hybrid functional (B3LYP)[18,19]. In these calculations we have employed 6-311g** basis set for
molecules having C and Si atoms and LanL2DZ basis set with effective core potential for other molecules. The plane wave ultrasoft pseudopotential calculations[17] were done with the local density approximation( LDA )[20, 21] employing a simple cubic supercell of 20 Å. The number of plane waves used in the calculation is set by energy cut-off( Ecute). We have used 287 eV Ecute for neutral and charged CH₄ molecules and 150 eV Ecute for other molecules. The use of supercell technique for charged systems causes electrostatic interaction within the images of supercells[22, 23]. Calculation of charged systems are efficiently handled in VASP by applying a background charge to maintain the charge neutrality and by adding dipole and quadrupole moment corrections[17]. The structure and ionization potential of SiH₄⁺ predicted by using this procedure are in close agreement with those of earlier calculations based on the HF, MP2 and LSDA methods[6, 8].

III. RESULTS AND DISCUSSION

A. Ground state structures

Fig. 1 shows the ground state structures of XH₄ molecules under neutral and charged states using the Gaussian98 package with BPW91 functional. We first discuss the ground state structures of the positively charged molecules. We see from the figure that the tetrahedral symmetry is broken when XH₄ molecules are ionized. The structure of CH₄⁺ has D₂d symmetry, while other positively charged molecules have Cₛ symmetry. We have investigated various possible symmetries of XH₄⁺ molecules and our results are summarized in Table. I. We see from the table that C₂v and D₂d structures of CH₄⁺ are very close in energy and differ only by 0.11 eV. The other positively charged molecules also have C₂v as the next higher energy structure. We could not find local minima of C₃v and Cₛ symmetries for CH₄⁺ and C₂v symmetry for SiH₄⁺ at the BPW91 level. These missing structures of CH₄⁺ and SiH₄⁺ molecules in our calculations have been studied earlier using different exchange-correlation potentials and different methods[4, 5, 6, 8, 15, 16] which show that these are not the ground state structures.

It is interesting to note that in the Cₛ symmetry, the positively charged molecules have a structure which is severely distorted from the tetrahedral structure. Furthermore, there is an unusual bonding between two hydrogen atoms. This bonding is confirmed by the charge
density calculation as shown in Fig. 2 which shows large electron density between the two hydrogen atoms of SiH$_4^+$. To ascertain that this is not an artifact of the BPW91 calculation, we have re-optimized the ground state structures using the HF and DFT methods with different exchange correlation functionals such as SPL and B3LYP. The H-H bond lengths obtained from various methods are essentially the same. This kind of over-coordination of hydrogen has also been observed in CH$_5^+$ [24, 25], SiH$_5^+$ [26] and small hydrogenated silicon clusters [27]. In Fig. 3, we have shown the total energy curve of SiH$_4^+$, H$_2$ and H$_2^+$ as a function of H-H distance. The total energy of SiH$_4^+$ is calculated by keeping Si-H bond length fixed but varying H-H bond distance. From the figure we see that the curvature of SiH$_4^+$ curve is smaller than H$_2$ and larger than H$_2^+$ curves. This shows H-H bond in SiH$_4^+$ is stronger than H$_2^+$ but weaker than H$_2$. Vibrational analysis also indicates that the H-H bond is sufficiently strong in these molecules. We see from Table. II that the force constant for H-H stretch mode of H-H pair is smaller than H$_2$ and larger than H$_2^+$ which implies that the strength of H-H bond is weaker than H$_2$ and stronger than H$_2^+$.

For the ground state structures of the negatively charged molecules, we note from Fig. 1 that the distortions of negatively charged molecules are different from those of positively charged molecules. XH$_4^-$ molecules have C$_{2v}$ symmetry except CH$_4^-$ which has tetrahedral symmetry. The two hydrogen atoms of XH$_4^-$ molecules are pushed away from each other which is in contrast to the H-H bond of XH$_4^+$ molecules with C$_s$ symmetry.

B. Stability

One may argue that the structure of XH$_4^+$ molecules with C$_s$ symmetry appears more like XH$_2^+$ and H$_2$ complex and hence unstable. Frey and Davidson [4] studied SiH$_4^+$ using CI singles root calculation and showed that C$_s$ structure is more stable than C$_{2v}$ against fragmentation into SiH$_2^+$ and H$_2$. We have calculated the fragmentation energy which is the energy required to fragment a XH$_4^+$ molecule into its binary products and has been calculated by taking the total energy difference between the XH$_4^+$ and the possible binary products. Of all the possible channels, the fragmentation of XH$_4^+$ into XH$_2^+$ and H$_2$ requires least energy. We give the fragmentation energies of XH$_4^+$ molecules for this process in Table. III. We see from the table that the energy required for the fragmentation of XH$_4^+$ into XH$_2^+$ and H$_2$ decreases for X=C to Pb. This means that the stability of XH$_4^+$ molecules decreases
from C to Pb molecules.

To examine the stability further we have done vibrational analysis of these molecules. In Table IV we present the vibrational frequencies of charged and neutral XH$_4$ molecules. Our calculated vibrational frequencies 880, 950, 2175 and 2192 cm$^{-1}$ of SiH$_4$ are in good agreement with those of experimentally obtained values$^{28}$ of 914, 953, 2189 and 2267 cm$^{-1}$. We see from the table that PbH$_4^+$ has a negative frequency and other molecules have only positive frequencies. Further, we see that one frequency is very low for C$_s$ symmetric XH$_4^+$ molecules and decreases from SiH$_4^+$ to GeH$_4^+$ and become negative for PbH$_4^+$.

The positive frequencies of a molecule indicate that the structure corresponds to an energy minimum. If one frequency is negative, the structure may be a transition state of the molecule$^{19}$. Since the frequency calculation is highly dependent on the method, the small negative frequency of PbH$_4^+$ may be an artifact of the method. To clarify this we have done vibrational analysis on re-optimized structures of C$_s$ symmetric XH$_4^+$ molecules using various methods. Calculation with the SPL exchange-correlation functional shows that one frequency of PbH$_4^+$ which was negative in the calculation with BPW91 functional is positive but near zero. Similarly, calculation with the UHF method also shows that all the frequencies of PbH$_4^+$ are positive. Irrespective of the sign of calculated frequencies, all these methods show that one vibrational mode of C$_s$ symmetric XH$_4^+$ molecules has a low frequency. Also we find that the force constant corresponding to this mode is nearly zero, which implies that the H atoms in this mode are moving on nearly flat potential energy surfaces.

We see from Fig. 1 that the mirror symmetry plane of C$_s$ structure is formed by the H-H pair and X atom. The vibrational mode with low frequency corresponds to the vibration of H-H pair about the mirror symmetry plane of C$_s$ structure. When the H-H pair vibrates about the plane, one atom of H-H pair moves in and the other moves out of the mirror plane without change in the H-H distance. Since the force constant is nearly zero for this vibration, the motion of H-H pair is more like an internal rotation about an axis which is perpendicular to the H-H bond and passing through the X atom. This internal rotation of H-H pair in XH$_4^+$ is similar to the internal rotation of O-H in CH$_3$OH molecule$^{29,30,31}$. Thus the low frequency mode in the present case does not indicate a transition state.
C. Effect of different occupations

Before proceeding further, we would like to resolve an interesting question regarding the occupation of degenerate states in charged tetrahedral XH$_4$ clusters. Let us ionize a charged XH$_4$ cluster keeping its tetrahedral structure intact. In this structure the HOMO is triply degenerate and is occupied by only 5 electrons. Hence, the HOMO of XH$_4^+$ is not completely filled. In such case of incompletely filled degenerate systems, there are many possible ways to fill the levels. The question is what is the right way of filling the levels and which distribution leads to the lowest energy. The usual practice in such situation is to fill all levels with fractional number of electrons, thereby keeping the symmetry intact.

To resolve the issue of occupation we have performed paramagnetic and spin-polarized calculations on tetrahedral SiH$_4^+$ and CH$_4^+$ using VASP package with local and non-local functionals for various possible electronic distributions. In paramagnetic calculations we have chosen two possible electronic distributions. The configuration with integer (2,2,1) occupation corresponds to asymmetric charge density and the other with fractional ($\frac{5}{3}$, $\frac{5}{3}$, $\frac{5}{3}$) occupation corresponds to symmetric charge density. Note that the spin multiplicity of SiH$_4^+$ and CH$_4^+$ is unity. The multiplicity is preserved in charge asymmetric configuration whereas it is zero for charge symmetric configuration. In spin-polarized calculations we have chosen three possible electronic configurations. The configuration with $\uparrow\uparrow\uparrow\downarrow$, $\uparrow\uparrow\uparrow\downarrow$, $\uparrow\uparrow\uparrow\downarrow$ ($\downarrow\downarrow\downarrow\downarrow$, $\downarrow\downarrow\downarrow\downarrow$, $\downarrow\downarrow\downarrow\downarrow$) occupation corresponds to charge symmetric density and multiplicity zero. Another configuration with $1\uparrow$, $1\uparrow$, $1\uparrow$ ($2\downarrow$, $2\downarrow$, $2\downarrow$) occupation also corresponds to symmetric charge density but multiplicity one. The other configuration with $1\uparrow$, $1\uparrow$, $1\uparrow$ ($1\downarrow$, $1\downarrow$, $0\downarrow$) occupation corresponds to asymmetric charge density and multiplicity one. We note that in all these configurations, the Kohn-Sham wave function is a single slater determinant. Hence the energy of the multiplet can be calculated directly using von Barth scheme\[32\]. The calculated total energy of tetrahedral SiH$_4^+$ and CH$_4^+$ molecules are summarized in Table. V.

From the table we see that paramagnetic calculations with local (LDA) and non-local (GGA) functionals do not give much difference between total energies of the molecules for symmetric and asymmetric charge density. On the other hand, the spin polarized calculations with local functional (LSD) favors charge symmetry for SiH$_4^+$ and charge asymmetry for CH$_4^+$. However, for both the molecules LSD calculations show that the symmetric charge
density which has multiplicity of zero is highly unfavored. We note that in spin polarized calculations the exchange interaction is taken care of more accurately than in paramagnetic calculations. Hence the unphysical zero multiplicity is strictly not favored by spin polarized calculations. But LSD does not give consistent results for multiplicity preserved symmetric and asymmetric charge density of SiH$_4^+$ and CH$_4^+$ molecules. This is a well known shortcoming of the LSD in the context of atomic calculations [33]. This deficiency of LSD is removed by the gradient corrected functionals [34]. We have therefore done spin polarized GGA (GGA-SP) calculations on SiH$_4^+$ and CH$_4^+$ molecules. Our calculations with GGA-SP functional give the consistent result that the asymmetric charge density is the ground state configuration for both SiH$_4^+$ and CH$_4^+$ molecules in tetrahedral structure.

Apart from the total energy calculation, one more important issue is the calculation of forces in such systems. We find that enforcing charge symmetry with fractional $\frac{5}{3}, \frac{5}{3}, \frac{5}{3}$ occupation in the degenerate level of XH$_4^+$ in LDA calculations does not distort the tetrahedral structure. This is in contrast with the structural relaxation of tetrahedral XH$_4^+$ with 2,2,1 occupation of degenerate level where the molecules results in distorted structure. Although LDA does not distinguish clearly the charge symmetric and asymmetric configurations, the calculated forces are different for the two configurations. This indicates that by enforcing symmetric charge distribution, the forces on atoms of XH$_4^+$ molecules are incorrectly estimated. It was also noted by Janak and Williams [33] that enforcing spherical charge distribution on atoms can give rise to errors in Hellman-Feynman forces. Therefore, our results clearly indicate that the electron charge density of tetrahedral XH$_4^+$ is asymmetric.

### D. Structural evolution

To gain insight into the mechanism of structural distortion in SiH$_4^+$ we look at the evolution of SiH$_4^+$ structure by using the VASP package with LDA functional and the conjugate gradient (CG) method [35]. We first ionize SiH$_4$ by holding atoms to obtain tetrahedral SiH$_4^+$ and then relax the structure. We find that with 64 steps the system rolls down from the initial tetrahedral to a well converged ground state structure. Each CG step corresponds to a particular geometrical configuration. The bond length between silicon atom and the distance between the hydrogen atoms as a function of CG steps are shown in Fig. 4(a). Initially one H atom moves away from the silicon atom and attains maximum Si-H bond length
of 1.92 Å at 8th step. Then this repelled H atom moves closer to the nearest hydrogen from 13th step which can be seen from the H-H distance shown in Fig. 4(b). The two hydrogen atoms come very close to each other to a distance of 0.84 Å and form an H-H pair. At this stage the structure of SiH$_4^+$ is C$_{2v}$. After 23rd step, this H-H pair gets rotated towards the other two hydrogen atoms without changing the H-H pair distance which finally results in $C_s$ symmetric SiH$_4^+$.

The summation of occupied Kohn-Sham orbital energies as a function of CG step is shown in the Fig. 4(c). From the figure we can see that the sum increases initially up to the 8th step and then decreases enormously between 13th and 23rd step. Then it fluctuates between 24 and 40th step and eventually converges to a constant value. The figure shows that the structural changes occurring from 13 and 23 are due to lowering in the orbital energies. Note that there is a minimum at 23rd step. As mentioned earlier at this CG step the structure of SiH$_4^+$ is C$_{2v}$ with the H-H bond. In a sense, the sum of orbital energies shown in the figure is similar to the Walsh diagram where one takes into account only the sum over orbital energies in predicting the structure. In Walsh diagram, each orbital energy is plotted as function of bond angle of a molecule. Then the minimum of the sum helps in predicting the structure. Thus in the present case the Walsh diagram would predict the symmetry of SiH$_4^+$ as C$_{2v}$ symmetry and not $C_s$, which is the correct symmetry.

E. Role of electrostatic interaction

We now show that the distortion and formation of H-H bond can be easily understood from arguments based on electrostatic interaction between atoms of the molecule. We first try to understand the structural evolution of SiH$_4^+$ as discussed in the previous subsection. Let us first consider neutral SiH$_4$ molecule. Since H is more electronegative than Si, the H atoms in SiH$_4$ has a small negative charge while Si will have a small positive charge. This is also shown by population analysis according to which each hydrogen atom holds a charge of -0.12e and silicon +0.52e. When the molecule is ionized to SiH$_4^+$ holding its atoms fixed, population analysis shows that the hydrogen atoms have -0.12e, -0.02e, +0.06e and +0.30e charge and silicon +0.77e charge. Interestingly, hydrogen atoms of tetrahedral SiH$_4^+$ do not have equal charge although the structure is symmetric. One hydrogen atom has more positive charge than the others and gets repelled by silicon atom which is also...
positively charged. This hydrogen moves away from the silicon to reduce the electrostatic repulsion and is attracted by the nearby hydrogen atom which has more electrons and forms an H-H bond. This H-H pair is positively charged and hence attracted by the nearby two hydrogen atoms which results in rotation of the pair towards the other two hydrogen atoms.

Since the electronegativities of Ge, Sn and Pb atoms are lower than that of hydrogen[37], GeH$_4^+$, SnH$_4^+$ and PbH$_4^+$ have distortions and bonds similar to that of SiH$_4^+$. However, as noted earlier, the structural distortion of CH$_4^+$ is different from that of SiH$_4^+$; two hydrogen atoms of CH$_4^+$ move away from each other which is in contrast with the formation of H-H bond in SiH$_4^+$. We now show that the same arguments based on electronegativity and electrostatic interaction also explain the structural distortion of CH$_4^+$. Since carbon has larger electronegativity than H atom, carbon in CH$_4$ will have negative charge while hydrogen will have positive charge. This is confirmed by population analysis which shows that a charge of -0.82e on carbon and +0.20e on each hydrogen atom. Ionizing CH$_4$ in the tetrahedral symmetric structure results in +0.20e, +0.23, +0.42e and +0.55e charge on H atoms and -0.40e charge on carbon. We see that the charge distribution is asymmetric and two hydrogen atoms are more positively charged than others. The two H atoms repel each other and open H-C-H bond angle as seen in Fig. 1.

Now we discuss the distortion of negatively charged molecules and explain it on the basis of the above arguments. We see from Fig. 1 that CH$_4^-$ has the tetrahedral symmetry while other negatively charged molecules have C$_2v$ symmetry. Putting an electron on CH$_4$ results in -1.00e on carbon and nearly zero electronic charge on H atoms. Because of this symmetrical charge distribution on hydrogen atoms, the forces on H atoms are radial and the structure of CH$_4^-$ remain tetrahedral. In contrast, in other molecules the charge on H atoms are not equal. For example, in SiH$_4^-$ population analysis shows a charge distribution of -0.14e, -0.15e, -0.16e and -0.37e on H atoms while silicon holds a charge of -0.18e. We can see that the H atom which is more negative gets repelled by other atoms. As a result, one of the H-Si-H bond angle opens up with the corresponding expansions in Si-H bond lengths. The trend in the electron distribution of GeH$_4^-$, SnH$_4^-$ and PbH$_4^-$ is similar to that of SiH$_4^-$. Therefore, the distortion of these molecules are similar to that of SiH$_4^-$ and can be explained using the same reasoning.
F. Charge asymmetry

It is interesting to note that in most of the charged molecules the symmetry is broken. We find that the symmetry breaking is associated with the creation of asymmetry in the charge distribution on H atoms upon charging. Removing or putting an electron on these molecules without changing the tetrahedral geometry may result in charge imbalance on H atoms or equal charges on H atoms as in the case of CH$_4^-$.

This charge imbalance or balance on H atoms depends on the electronic structure of the molecule. In particular, on the nature and occupation of the HOMO.

Using molecular orbital theory we discuss the nature of HOMO in these molecules and show how it contributes to charge distribution among H atoms. In Fig. 5, we show the MO construction of XH$_4$ from linear combinations of atomic orbitals. As shown in the figure, there are eight MOs, the lower four are bonding states and the upper four are antibonding states. The bonding and antibonding states have either $A_1$ symmetry or $T_2$ symmetry. $A_1$ level is non-degenerate while $T_2$ level is triply degenerate. While the bonding energy level of $A_1$ symmetry is always lower in energy than $T_2$, the order of antibonding levels depends on the molecule. For CH$_4$ antibonding $A_1$ level is lower in energy than $T_2$ while for SiH$_4$, GeH$_4$, SnH$_4$ and PbH$_4$ antibonding $T_2$ level is lower than $A_1$. From the figure we can see that the MO with $A_1$ symmetry is a linear combination of valance atomic s orbitals of X and H atoms. The MO with $T_2$ symmetry is a linear combination of valance p orbitals of X and s orbitals of H atoms. Because of mixing between p and s character, $T_2$ orbitals have strong directionality along H atoms. If $T_2$ orbital is fully occupied, it has equal weight along H atoms and results in a uniform charge distribution on H atoms as in the case of neutral XH$_4$ molecules. If $T_2$ orbital is incompletely filled with unequal electrons, it has unequal weight along H atoms and results in a non-uniform charge distribution on H atoms.

Removing an electron from tetrahedral XH$_4$ results with 5 electrons and the $T_2$ orbital is incompletely filled. Hence the charges on H atoms of tetrahedral XH$_4^+$ molecules are not equal. This can be seen from Fig. 6(a) and (b) which show the charge densities of SiH$_4$ and SiH$_4^+$ in tetrahedral structure. We see from the figure that while the charge densities on H atoms of SiH$_4$ are same, the charge densities on H atoms of SiH$_4^+$ are different. In the case of negatively charged molecules the HOMO can be of $T_2$ or $A_1$ symmetry. The HOMO of CH$_4^-$ has $A_1$ symmetry. Since $A_1$ is a linear combination of valance s atomic orbitals with

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equal weights from hydrogen atoms, the charge distribution is equal on H atoms of CH$_4^-$ as shown in Fig. 6(c). The higher electron density around the carbon atom as seen in the figure can be attributed to the higher electronegativity of carbon compared to hydrogen. The HOMO of other negatively charged molecules has T$_2$ symmetry and is singly occupied. This leads to asymmetric charge distribution on H atoms. Note that since A$_1$ level in CH$_4^-$ is non-degenerate, CH$_4^-$ does not show the Jahn-Teller effect, and also no charge asymmetry. On the other hand, if the HOMO has T$_2$ symmetry and is not completely occupied as in the case of SiH$_4^+$, the molecule will show the Jahn-Teller effect and the charge asymmetry. This implies that the creation of the charge asymmetry and the Jahn-Teller effect are intimately connected.

IV. CONCLUSIONS

We have investigated the ground state structures of neutral and charged XH$_4$ molecules using first principle electronic structure methods. We find that charging XH$_4$ molecules can break the symmetry and change their structures drastically. Negatively charged molecules are distorted by pushing two hydrogen atoms away from each other while the positively charged molecules get distorted with an unusual H-H bond formation except for X=C. The calculations done by various methods and the charge density analysis confirm the existence of H-H bond. Furthermore, vibrational analysis shows that the strength of H-H bond in the positively charged molecule is stronger than H$_2^+$ and weaker than H$_2$. We find that one vibrational mode of C$_s$ symmetric XH$_4^+$ molecules has low frequency and corresponds to internal rotation of the H-H pair. Our vibrational analysis indicates that the molecules are not transition states. The fragmentation behavior of XH$_4^+$ into XH$_2$ and H$_2$ shows that the stability decreases from CH$_4^+$ to PbH$_4^+$.

From the total energy calculations using LDA, LSD, GGA and GGA-SP functionals we have shown that the ground state electronic structure of a charged tetrahedral molecule has asymmetric charge density corresponding to integer occupation. We have provided an insight into the symmetry breaking and shown that the distortion and unusual H-H bond formation can be understood easily using simple arguments based on charge asymmetry and electrostatic interaction between the atoms. Unequal charges on hydrogen atoms give rise to different electrostatic forces on different atoms and lead to distortion. On the other hand
if the charges are equal on hydrogen atoms, the structural symmetry of the molecule will be preserved. We have shown how the charge asymmetry arises due to character of the HOMO and eventually leads to the symmetry breaking.

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[35] We have also looked at the evolution of SiH$_4^+$ structure using the steepest descent method. Although the convergence is slow, the results are similar to those shown in Fig. 4.

[36] See, for example, I. N. Levine, Quantum Chemistry (Prentice-Hall, Englewood Cliffs, New Jersey, 1991) p. 503-506.

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[38] The numbers shown in the text are obtained from the natural population analysis using
BPW91 exchange correlation potential. The numbers obtained by the Mulliken analysis are somewhat different but show the same trend and thus do not change our conclusions.

[39] See, for example, A. A. Levin, *Solid State Quantum Chemistry* (McGraw Hill Book Company, New York, 1977) p. 34.
FIGURE CAPTIONS

Fig. 1. Ground state structures of neutral and charged XH$_4$ molecules.

Fig. 2. Electron density contour of SiH$_4^+$ in the plane of Si and the two bonded H atoms.

Fig. 3. The total energy of SiH$_4^+$, H$_2$ and H$_2^+$ molecules as a function of H-H distance. The total energy of the molecule is given with respect its ground state energy.

Fig. 4. (a) The Si-H bond lengths and (b) H-H distances in SiH$_4^+$ as a function of CG steps. The H atoms have the same label as those of SiH$_4^+$ in Fig. 1. (c) The sum of energy levels of SiH$_4^+$ as a function of CG steps.

Fig. 5. A schematic energy-level diagram showing the construction of molecular orbitals of XH$_4$ molecule from atomic orbitals. The levels on the extreme left side are the valence states of X atoms and the level on the extreme right is the valence state of H atom. The levels which are in the center are the molecular states of XH$_4$.

Fig. 6. The isosurface contour of valence electrons of (a) SiH$_4$ (b) SiH$_4^+$ and (c) CH$_4^-$ obtained by using the Gaussian package. The value of the contour is chosen such that one able to distinguish the difference between the charge density on the H atoms. The densities shown in figure have the contour value of 0.20 for SiH$_4$ and SiH$_4^+$ molecules and 0.3 for CH$_4^-$.
Table. I. Relative energies (in eV) of XH$_4^+$ molecules for various symmetries with respect to the ground state structures. The results are obtained using the Gaussian98 with the BPW91 exchange-correlation functional.

|         | C$_{2v}$ | D$_{2d}$ | C$_{3v}$ | C$_s$ |
|---------|----------|----------|----------|-------|
| CH$_4^+$| 0.11     | 0        | -        | -     |
| SiH$_4^+$| -       | 0.73     | 0.73     | 0     |
| GeH$_4^+$| 0.83    | 0.94     | 0.87     | 0     |
| SnH$_4^+$| 1.36    | 1.46     | 1.35     | 0     |
| PbH$_4^+$| 1.80    | 1.91     | 1.72     | 0     |

Table. II Properties of H-H bond calculated using the Gaussian98 package with the BPW91 exchange-correlation functional.

|                  | SiH$_4^+$ | GeH$_4^+$ | SnH$_4^+$ | PbH$_4^+$ | H$_2$ | H$_2^+$ |
|------------------|-----------|-----------|-----------|-----------|-------|---------|
| H-H bond length(Å) | 0.80      | 0.78      | 0.77      | 0.76      | 0.75  | 1.12    |
| H-H frequency(cm$^{-1}$) | 3598     | 3911      | 4061      | 4134      | 4349  | 1976    |
| H-H force constant(eV/Å) | 7.69     | 9.08      | 9.79      | 10.15     | 11.23 | 2.32    |

Table. III. The energy required to fragment XH$_4^+$ into XH$_2^+$ and H$_2$. The results are obtained using the Gaussian98 package with the BPW91 exchange-correlation functional.

| Reactant | product 1 | product 2 | Fragmentation energy(eV) |
|----------|-----------|-----------|--------------------------|
| CH$_4^+$ | CH$_2^+$  | H$_2$     | 3.03                     |
| SiH$_4^+$| SiH$_2^+$ | H$_2$     | 0.69                     |
| GeH$_4^+$| GeH$_2^+$ | H$_2$     | 0.42                     |
| SnH$_4^+$| SnH$_2^+$ | H$_2$     | 0.28                     |
| PbH$_4^+$| PbH$_2^+$ | H$_2$     | 0.21                     |
Table IV The calculated vibrational frequencies $\nu$ (in cm$^{-1}$) and force constant k (in eV/Å) of neutral and charged XH$_4$ molecules using the Gaussian98 package with the BPW91 exchange-correlation potential.

|                | Neutral molecules | Positively charged molecules |
|----------------|------------------|-----------------------------|
|                | CH$_4$ | SiH$_4$ | GeH$_4$ | SnH$_4$ | PbH$_4$ | CH$_4^+$ | SiH$_4^+$ | GeH$_4^+$ | SnH$_4^+$ | PbH$_4^+$ |
|                | $\nu$  | k    | $\nu$  | k    | $\nu$  | k    | $\nu$  | k    | $\nu$  | k    |
| 1              | 1298  | 1.17 | 879   | 0.50 | 788   | 0.38 | 676   | 0.28 | 644   | 0.25 |
| 2              | 1298  | 1.17 | 880   | 0.50 | 788   | 0.38 | 676   | 0.28 | 644   | 0.25 |
| 3              | 1298  | 1.17 | 881   | 0.50 | 788   | 0.38 | 676   | 0.28 | 644   | 0.25 |
| 4              | 1521  | 1.37 | 949   | 0.53 | 901   | 0.48 | 735   | 0.32 | 703   | 0.29 |
| 5              | 1521  | 1.37 | 950   | 0.54 | 901   | 0.48 | 735   | 0.32 | 703   | 0.29 |
| 6              | 2975  | 5.26 | 2175  | 2.81 | 2058  | 2.51 | 1856  | 2.05 | 1769  | 1.86 |
| 7              | 3090  | 6.19 | 2191  | 2.97 | 2071  | 2.59 | 1856  | 2.07 | 1786  | 1.91 |
| 8              | 3090  | 6.19 | 2191  | 2.97 | 2072  | 2.59 | 1857  | 2.07 | 1786  | 1.91 |
| 9              | 3090  | 6.19 | 2191  | 2.97 | 2072  | 2.59 | 1857  | 2.07 | 1787  | 1.91 |
|                | $\nu$  | k    | $\nu$  | k    | $\nu$  | k    | $\nu$  | k    | $\nu$  | k    |
| 1              | 470   | 0.15 | 256   | 0.04 | 136   | 0.01 | 46    | 0.00 | -104  | 0.01 |
| 2              | 471   | 0.15 | 616   | 0.25 | 510   | 0.16 | 380   | 0.09 | 316   | 0.06 |
| 3              | 1022  | 0.78 | 680   | 0.28 | 532   | 0.17 | 394   | 0.09 | 339   | 0.07 |
| 4              | 1253  | 0.93 | 766   | 0.35 | 542   | 0.18 | 430   | 0.11 | 396   | 0.09 |
| 5              | 1420  | 1.20 | 850   | 0.45 | 658   | 0.26 | 495   | 0.15 | 425   | 0.11 |
| 6              | 2642  | 4.26 | 1077  | 0.69 | 781   | 0.37 | 666   | 0.27 | 631   | 0.24 |
| 7              | 2758  | 4.52 | 2164  | 2.83 | 1957  | 2.29 | 1729  | 1.78 | 1506  | 1.35 |
| 8              | 2851  | 5.32 | 2242  | 3.15 | 2046  | 2.54 | 1807  | 1.96 | 1623  | 1.57 |
| 9              | 2852  | 5.32 | 3598  | 7.69 | 3911  | 9.08 | 4061  | 9.79 | 4134  | 10.15 |
| Negatively charged molecules | CH$_4^-$ | SiH$_4^-$ | GeH$_4^-$ | SnH$_4^-$ | PbH$_4^-$ |
|-----------------------------|---------|---------|---------|---------|---------|
| ν k | ν k | ν k | ν k | ν k | ν k |
| 1 1133 0.88 | 690 0.30 | 614 0.23 | 491 0.15 | 347 0.07 |
| 2 1133 0.88 | 759 0.36 | 729 0.33 | 619 0.23 | 469 0.13 |
| 3 1133 0.88 | 790 0.38 | 768 0.35 | 645 0.25 | 673 0.27 |
| 4 1372 1.12 | 955 0.58 | 884 0.48 | 784 0.37 | 675 0.27 |
| 5 1372 1.12 | 1000 0.59 | 934 0.52 | 794 0.37 | 692 0.29 |
| 6 2537 3.82 | 1323 1.09 | 1099 0.73 | 1067 0.68 | 766 0.35 |
| 7 2631 4.55 | 1429 1.22 | 1323 1.04 | 1245 0.92 | 1124 0.75 |
| 8 2631 4.55 | 1958 2.32 | 1786 1.91 | 1607 1.54 | 1472 1.29 |
| 9 2631 4.55 | 1962 2.37 | 1804 1.96 | 1615 1.56 | 1489 1.32 |
Table. V Relative energies (in eV) of SiH$_4^+$ and CH$_4^+$ in tetrahedral structure for various electronic configuration with respect to charge asymmetric configuration, using different exchange-correlation functionals.

| configuration                  | SiH$_4^+$ | CH$_4^+$ |
|-------------------------------|-----------|----------|
| LDA 2, 2, 1                  | 0.000     | 0.000    |
| $\frac{5}{3}, \frac{5}{3}, \frac{5}{3}$ | 0.001     | 0.001    |
| GGA 2, 2, 1                  | 0.000     | 0.000    |
| $\frac{5}{3}, \frac{5}{3}, \frac{5}{3}$ | 0.030     | 0.000    |
| LSD $1\uparrow, 1\uparrow, 1\uparrow(1\downarrow, 1\downarrow, 0\downarrow)$ | 0.000     | 0.000    |
| $\frac{5}{3}\uparrow, \frac{5}{3}\uparrow, \frac{5}{3}\uparrow(\frac{5}{3}\downarrow, \frac{5}{3}\downarrow, \frac{5}{3}\downarrow)$ | 0.139     | 0.296    |
| $1\uparrow, 1\uparrow, 1\uparrow(\frac{5}{3}\downarrow, \frac{5}{3}\downarrow, \frac{5}{3}\downarrow)$ | -0.028    | 0.036    |
| GGA-SP $1\uparrow, 1\uparrow, 1\uparrow(1\downarrow, 1\downarrow, 0\downarrow)$ | 0.000     | 0.000    |
| $\frac{5}{3}\uparrow, \frac{5}{3}\uparrow, \frac{5}{3}\uparrow(\frac{5}{3}\downarrow, \frac{5}{3}\downarrow, \frac{5}{3}\downarrow)$ | 0.215     | 0.333    |
| $1\uparrow, 1\uparrow, 1\uparrow(\frac{5}{3}\downarrow, \frac{5}{3}\downarrow, \frac{5}{3}\downarrow)$ | 0.070     | 0.105    |
Energy sum of occupied levels

(a) 
Si–H4
Si–H3
Si–H1, Si–H2

(b) 
H1–H2
H3–H4

(c) 
Energy sum of occupied levels

Si–H bondlengths (Å)

-112
-108
-104

1.5
1.7
1.9

CG steps

Energy (eV) H–H distance (Å)
\[ \text{SiH}_4 \quad \text{(a)} \]

\[ \text{SiH}_4^+ \quad \text{(b)} \]

\[ \text{CH}_4^- \quad \text{(c)} \]