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The intermolecular weak interaction in the GeH_4•••Y(Y=He, Ne, Ar and Kr) complexes

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ABSTRACT

MP2/aug-cc-pvtz level was used to optimize geometries of the complexes between GeH_4 and Y(Y=He, Ne, Ar, Kr) have been calculated at the. The structures and electronic properties of the blue-shift hydrogen bonds complexes GeH_4…Y(Y=Ar, Kr) were investigated. The calculated interaction energies with basis set super-position error (BSSE) correction revealed that the relative stabilities of the complexes in the order: GeH_4…He $< GeH_4$…Ne $< GeH_4$…Ar $\approx GeH_4$…Kr. The calculated results showed that the interactions between GeH_4 and Y(Y=He, Ne) belong to van der Waals force, and those between GeH_4 and Y(Y=Ar, Kr) belong to weak hydrogen bond. NBO (natural bond orbital theory) and electron behavior analysis showed that GeH_4…Y(Y= Ar, Kr) hydrogen bond is with a non-electrostatic property. Electron density topological properties have also been calculated to investigate the critical points of H…Y weak bonds in all the structures of the complexes.
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INTRODUCTION

Noncovalent weak interactions have important roles in the field of molecule recognition, in biochemical processes, arrangement of molecules in crystals and in materials science. These interactions have captured the interest of chemists for a long time, and studies of their theories and experiments have been well reported[1, 2]. It has been found that many physical and chemical phenomena are closely related to intermolecular noncovalent weak interactions including dihydrogen bonds[3], halogen bonds[4], ð–cation interactions[5]. Of course, hy-

drogen bonds are the most studied among all the noncovalent weak interactions. Under certain conditions an atom of hydrogen in attracted by rather strong forces to two atoms, instead of only one, so that it may be considered to be acting as a bond between them. This is so-called the hydrogen bond[6], which is a common noncovalent weak interaction besides of van der Waals force. Pauling pointed out that in a hydrogen bond system, the hydrogen atom is situated only between the most electronegative atoms and it usually interacts much stronger with one of them[7]. That is to say, the interaction between hydrogen and another elec-

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tronegative atom is much weaker and mostly electrostatic in nature. However, when a hydrogen atom covalently bonds to a weak electropositive atom situated in the middle of the two weak electropositive atoms, even in the middle of a weak electropositive atom and an electrically neutral atom, what a molecule interactions will be? The hydrogen bond would be formed or not? What the nature and the electronic behavior of the interaction will be? Based on these ideas, we are interested in whether there are any noncovalent weak interactions like hydrogen bond or van der Waals force, and how the interactions take place. We consider a particular set of molecule complexes formed by GeH_4 and Y(Y=He, Ne, Ar, Kr), as shown in Figure 1, where the hydrogen atom covalently binding to Ge atom situated in the middle of Ge and rare gas atoms Y(Y=He, Ne, Ar, Kr), Thus, the nature and electron structures of the weak interactions between them were investigated and characterized using the second–order Møller–Plesset (MP2) theoretical method.

COMPUTATIONAL DETAILS

All the monomers and complexes were optimized by using the second-order Møller-Plesset (MP2) methods, respectively. And the aug-cc-pvtz was used as the calculated basis set. This method and basis set adequately describes noncovalent interaction systems in recent years[8, 9], so it is reliable for the purpose of our study. The interaction energies were corrected with the basis set superposition error (BSSE). The BSSE was evaluated by using the counterpoise method of Boys and Bernardi[10]. The calculations of the electron density topological properties were carried out with the AIM 2000 program[11]. The NBO analyses were carried out with the NBO 5.0 package[12]. All other calculations were performed with the Gaussian 03 program[13].

RESULTS AND DISCUSSION

Geometric configurations

The optimized geometric configurations on the potential surfaces of the monomer and $GeH_4\ldots$Y(Y=He, Ne, Ar, Kr) complexes are shown in Figure 1, and some
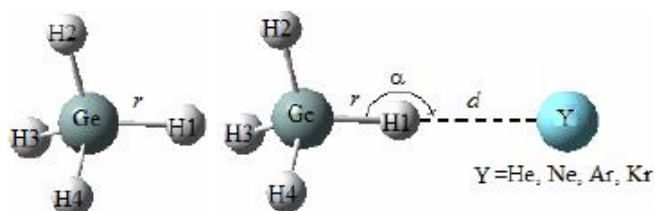

Figure 1 : The geometric configurations of the monomer and complexes

important structural parameters obtained at the MP2/aug-cc-pvtz computational level are listed in TABLE 1. As shown in Figure 1, the weak interaction systems formed via Y(Y=He, Ne, Ar, Kr) atoms interacting directly with H1 atom of the GeH_4 monomer. Comparing parameters of the moieties with those of the complexes given in TABLE 1, it can be easily found that the Ge-H1 bond lengths all decreased to some degree after complex formation. For example, the Ge-H1 bond lengths decreased only by 0.0001, 0.0002, 0.0002, and 0.0003 Å in the complexes $GeH_4\ldots$He, $GeH_4\ldots$Ne, $GeH_4\ldots$Ar and $GeH_4\ldots$Kr, respectively. This predicts that the interaction energies would be small. The van der Waals radius is an important factor in investigating the geometric structure. If the distance between two atoms is less than the sum of their van der Waals radius, a certain degree of weak interaction like hydrogen bonding, which is stronger than van der Waals forces, exists between the two atoms. If the distance between two atoms is larger than the sum of their van der Waals radius, a van der Waals complex forms. The van der Waals radii experimental value of the H atom is 1.20Å, and these of He, Ne, Ar and Kr atoms are 1.40, 1.54, 1.88 and 2.02 Å, respectively. From TABLE 1, it can be found that the distances between H1 and Y (Y=He, Ne) obviously larger than the sum of their van der Waals radii. So we can conclude that $GeH_4\ldots$He and $GeH_4\ldots$Ne systems belong to van der Waals complexes. However, the distances between H1 and Y (Y=Ar, Kr) obviously less than the sum of their van der Waals radii in the $GeH_4\ldots$Y (Y=Ar, Kr) systems, so $GeH_4\ldots$Ar and $GeH_4\ldots$Kr can be regard as like-hydrogen-bond complexes in geometric characteristic. Further more, Ge-H1$\ldots$Y(Y=He, Ne, Ar, Kr) bond angle is another bond parameter characteristic necessary to investigate. In generally, hydrogen bonds have the line structure potential in geometric configuration, which is decided by the n>σ* electron behavior of the

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hydrogen bonds. So, the stronger the hydrogen bond, the more the bond angle close to 180°. For example, the bond angle is about 175-180° in much strong hydrogen bonds, 130-180° in strong hydrogen bonds and 90-180° in weak hydrogen bonds[6]. As for GeH_4…Y (Y=He, Ne, Ar, Kr) systems, Ge-H1-Y(Y=He, Ne, Ar, Kr) bond angles are all 180°, so, it is suitable to form hydrogen bonds structures between GeH_4 and Y (Y=He, Ne, Ar, Kr) if only geometric characteristic was considered.

TABLE 1 : Geometrical parameters (Å, °) of the complexes obtained (r, d and α are defined in the Figure 1)

Compound	MP2/aug-cc-pvtz		
	r	d	α
GeH_4	1.5118	–	–
GeH_4···He	1.5117	2.886	180.0
GeH_4···Ne	1.5116	2.779	180.0
GeH_4···Ar	1.5116	3.086	180.0
GeH_4···Kr	1.5115	3.089	180.0

Interaction energies and frequency analysis

Interaction energy is a powerful approach for estimating the strength of an intermolecular interaction. The interaction energies in the GeH_4…Y (Y=He, Ne, Ar, Kr) systems at MP2/ aug-cc-pvtz level are listed in TABLE 2. The BSSE correction is taken into consideration because this is a necessary step for accurately describing the energies of weak interaction systems. As shown in TABLE 2, the BSSE-corrected interaction energies (ΔE_{CP}) are -0.08 and -0.13 kJ/mol in GeH_4…He and GeH_4…Ne, respectively, which are obviously less than those of GeH_4…Ar and GeH_4…Kr complexes. And the ΔE_{CP} in GeH_4…Ar is close to that of GeH_4…Kr. These suggest that GeH_4 is easier to bind with Ar and Kr than with He and Ne. Comparing the BSSE corrected interaction energies (ΔE_{CP}) of the GeH_4…Y (Y=He, Ne, Ar, Kr) systems, it can be easily found that the relative stabilities of the four complexes increased in the order: GeH_4…He < GeH_4…Ne < GeH_4…Ar ≈ GeH_4…Kr. Further more, we noted that the ÄE in the GeH_4…Y(Y=He, Ne) systems are only -0.45 and -1.05 kJ/mol, respectively. So, the interactions between GeH_4 and Y(Y=He, Ne) are very weak, and can be classified to van der Waals forces. However, the ΔE in the GeH_4…Y(Y=Ar, Kr) systems

are about 2.0 ~ 4.0 kJ/mol. So, the GeH_4…Ar and GeH_4…Kr can be considered as hydrogen bond complexes. In total, the intermolecular interactions between GeH_4 and He, Ne, Ar, Kr are van der Waals forces to hydrogen bond complexes consequently.

To help possible experimental identification of the

TABLE 2 : Symmetry group, PG, and BSSE corrected interaction energy (kJ/mol) for the three complexes at the MP2/aug-cc-pvtz computational levels

complexes	PG	ΔE	BSSE	ΔE_{CP}
GeH_4···He	*C3v*	-0.45	0.37	-0.08
GeH_4···Ne	*C3v*	-1.05	0.92	-0.13
GeH_4···Ar	*C3v*	-2.22	1.37	-0.85
GeH_4···Kr	*C3v*	-3.85	3.02	-0.83

intermolecular weak interactions described in this work, TABLE 3 showed the corresponding bond (Ge-H1) stretching intensities and frequencies of monomer and complexes calculated at MP2/aug-cc-pvtz level. From TABLE 2, compared to GeH_4 monomer, the stretching frequencies of the Ge-H1 bonds in the complexes present some degree of blue-shift. For example, the blue-shift of the Ge-H1 bonds are 3.78, 6.68, 8.88 and 11.34 cm⁻¹ in GeH_4···He, GeH_4··Ne, GeH_4··Ar and GeH_4···Kr complexes, respectively. Namely, the blue-shift values of the Ge-H1 bonds increased consequently from GeH_4···He to GeH_4···Kr. In addition, compared to GeH_4, the Ge-H1 stretching intensities all decreased after the formation of the complexes. This attribute to the decrease of the Ge-H1 bonds polarities when the complexes formed, and this kind of weaker polarity produced less dipolar under the same inter-atoms displacement. It is worth to noted that the existences of the H1···Y (Y=He, Ne, Ar, Kr) stretching vibrational frequencies based on the whole complexes despite of their small stretching vibrational intensities. This is also

TABLE 3 : Stretch vibrational frequency (υ, cm⁻¹), frequency shift ($\Delta\upsilon$, cm⁻¹), and IR intensity (km•mol⁻¹) of the Ge -H1 bond.

Compound	υ_{Ge-H1}	IR intensity	$\Delta\upsilon_{Ge-H1}$	$\upsilon_{H1···Y}$
GeH_4	2292.02	127.38	–	–
GeH_4···He	2295.80	122.71	3.78	29.97(0.007)
GeH_4···Ne	2298.70	117.15	6.68	23.76(0.008)
GeH_4···Ar	2300.90	116.5	8.88	31.31(0.009)
GeH_4···Kr	2303.36	112.96	11.34	31.46(0.010)

one of the theoretical testimonies for the existences of the weak intermolecular interactions between GeH_4 and Y (Y=He, Ne, Ar, Kr).

NBO analysis and NMR properties

For a better understanding of the mechanism of formation of complexes, NBO analysis was performed for the monomer and complexes at MP2/ aug-cc-pvtz level, and the corresponding results are listed in TABLE 4. The interaction strength between the monomers could be clarified according to the second-order stabilization energy $E_{ij}^{(2)}$ obtained from the NBO analysis as follows:

$$\mathbf{E_{ij}}^{(2)} = -\eta_\sigma \frac{\langle \sigma* |\mathbf{F}| \sigma \rangle}{\varepsilon_{\sigma*} - \varepsilon_\sigma} = \eta_\sigma \frac{\mathbf{F_{ij}}^2}{\Delta \mathbf{E}}$$

Where F_{ij} is the Fock matrix element between the i and j NBO orbitals, ε_σ and $\varepsilon_{\sigma*}$ are the energies of σ and $\sigma*$, and η_σ is the population of the donor σ orbital. As NBO theory indicates, electron transfer among orbitals accompanies the formation of a noncovalent bond and has a major role in the formation, so the $E_{ij}^{(2)}$ can be taken as an index to judge the strength of a noncovalent interaction. Generally, the larger the stabilization energy $E_{ij}^{(2)}$, the stronger the interaction between the donor and acceptor orbitals. As shown in TABLE 4, there is only one kind of charge transfer in the $GeH_4 \cdots Y(Y=Ne, Ar, Kr)$ complexes, namely LP4(Y) $\rightarrow \sigma*$(Ge-H1) (Figure 2), and the related second stabilization energy $E_{ij}^{(2)}$ are about 0.2 ~ 2.0 kJ•mol^{-1}. However, there is no corresponding LP4(He) $\rightarrow \sigma*$(Ge-H1) charge transfer in the $GeH_4 \cdots$ He complex. The overlap between donor orbital and acceptor orbital is the characteristic of the hydrogen bond interaction. It can be seen from Figure 2 that there is no obvious and effective orbital overlap between LP4(Ne) and $\sigma*$(Ge-H1) despite of the existence of the LP4(Ne)$\rightarrow$ $\sigma*$(Ge-H1) charge transfer in the $GeH_4 \cdots$ Ne complex. So, different from $GeH_4 \cdots$ Ar and $GeH_4 \cdots$ Kr, $GeH_4 \cdots$ He and $GeH_4 \cdots$ Ne are impossible hydrogen bond complexes. The charge transfers between natural bond orbitals lead to the decrease of the charge population of the (Ge-H1) bond orbital or increase of the charge population of the $\sigma*$(Ge-H1) anti-bond orbital. For example, the charge population of the $\sigma*$ (Ge-H1) increased by 0.01, 0.15, 0.59 and 1.17 me in the

$GeH_4 \cdots$ He, $GeH_4 \cdots$ Ne, $GeH_4 \cdots$ Ar and $GeH_4 \cdots$ Kr, respectively. Additionally, the Mulliken charge flow from Y(Y=He, Ne, Ar, Kr) to GeH_4 are 1, 6, 3 and 3 me in the four complexes, respectively. The dipolar of the four complexes are also listed in TABLE 4. The dipolar of the GeH_4 and Y(Y=He, Ne, Ar, Kr) are all zero, but the dipolar of all the complexes are not zero. This suggests the electron distributions of the systems changed after the complex formed, namely, the symmetry of the electron distributions decreased. The charge population analysis manifests the charge population of the H atom in GeH_4 monomer is negative, but it still may form complexes with hydrogen bonds geometric characteristic with neutral atoms like Ar and Kr. So, the $GeH_4 \cdots$ Ar and $GeH_4 \cdots$ Kr hydrogen bonds studied here different from the traditional hydrogen bonds. $GeH_4 \cdots$ Y(Y= Ar, Kr) hydrogen bonds have no electrostatic property while the traditional hydrogen bonds have. They are probably of non-electrostatic weak interactions which are brought by the electron-delocalization-assisted processing.

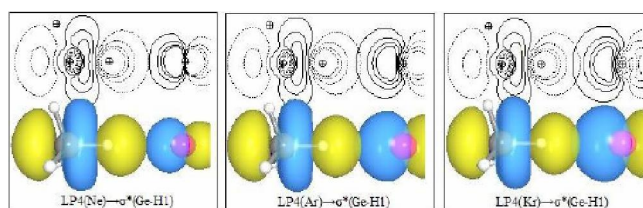In order to further investigate the flow direction of

Figure 2 : 3D images of the LP4(Y)$\rightarrow\sigma*$(Ge-H1) (Y= Ne, Ar, Kr) natural bond orbital interactions

TABLE 4 : NBO analysis for the complexes at the MP2/aug-cc-pvtz level

	$GeH_4 \cdots$He	$GeH_4 \cdots$Ne	$GeH_4 \cdots$Ar	$GeH_4 \cdots$Kr
$E_{ij}^{(2)}$LP4 (Y)$\rightarrow\sigma*$ (Ge-H1) kJ/mol	-	0.59	1.72	3.02
Δ_{MC}/me(Y$\rightarrow$ (GeH$_4$))	1	6	3	3
Δ_{NBC}/me(Y$\rightarrow\sigma*$ (Ge-H1))	0.01	0.15	0.59	1.17
Dipole moments/Debye	0.0084	0.0229	0.0198	0.0205

the electrons in the four complexes, all the atoms' chemical shifts in the GeH_4 obtained at the MP2/aug-cc-pvtz

computational level are given in TABLE 5. Comparing the GeH_4 monomer with GeH_4 moiety of the complexes, the relative chemical shifts of the non-involved H (H2, H3 and H4) atoms all decreased by a certain degree, and presented a trend to upfield, however, the relative chemical shift of involved H atom (H1) increased and presented a trend to downfield. The absolute chemical shift of Ge atom increased when complexes formed. These indicated that the electrons flow from Y(Y=He, Ne, Ar, Kr) moiety to GeH_4 moiety.

TABLE 5 : Variation of the relative chemical shifts (ppm) of the GeH_4 upon complexation at the MP2/aug-cc-pvtz computational level

Compound	H1	Ge	H(2, 3, 4)
GeH_4	3.895	1822.64(absolut)	3.895
$GeH_4\cdots He$	3.895	1823.22	3.883
$GeH_4\cdots Ne$	3.907	1823.97	3.883
$GeH_4\cdots Ar$	3.978	1824.22	3.883
$GeH_4\cdots Kr$	4.073	1824.63	3.871

Molecules electrostatic potential and electron density topological analysis

The molecules electrostatic potential (MESP) image is one of the tools for conformational analysis. It has been used primarily for the studies of biological recognition and hydrogen bonding interactions[14, 15]. The electrostatic potential (ε_p) is defined as being the energy of interaction of a positive point charge with the nuclei and the electrons of a molecule[16]:

$$\varepsilon_P = \sum_A^{nucleus} \frac{Z_A}{R_{AP}} - \sum_\mu^{base\ function} \sum_\nu P_{\mu\nu} \int \frac{\phi_\mu(r)\phi_\nu(r)}{r_P} dr$$

The first summation is that of nucleus A. The Z terms are the atomic numbers and R_{Ap} are the distances between the nuclei and the pints charge. The second part of the summation is the basis functions ϕ. P is the density matrix, and the integrals reflect Coulombic interactions between the electrons and the point charge, where r_P is the distance between them. Positive potential values reflect nucleus predominance, while negative values represent rearrangements of electronic charges and lone pairs of electrons. The fundamental application of this study is the analysis of non-covalent interactions. Figure 3 plots the 3D images of the molecular complexes electrostatic potential of the $GeH_4\ldots$Ar system.

As shown in Figure 3, the positive electrostatic potential in blue color distributes in the region both out side of Ar nuclear and out side of H1 nuclear. We know Ar and H1 are the direct interaction atoms pair. This also suggests the view of the non-electrostatic weak interaction in nature of the $GeH_4\ldots$Y(Y=Ar, Kr) systems described in part of NBO analysis.
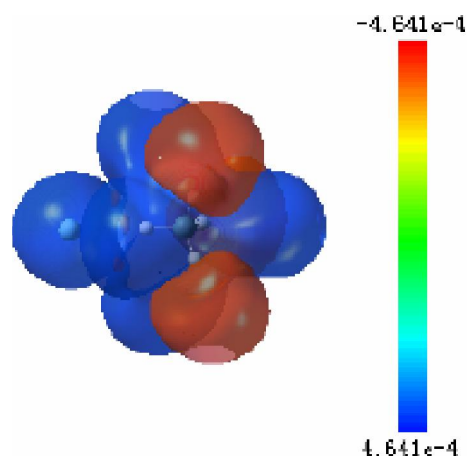

Figure 3 : 3D molecules electrostatic potential distribution of the $GeH_4\ldots$Ar complexes

TABLE 6 : Electron density topological properties of H1$\cdots$Y bond critical points

Compound	Atom pair	$\rho(r_c)$/a.u.	λ_1	Λ_2	λ_3	$\nabla^2\rho(r_c)$ /a.u.	ε
$GeH_4\cdots He$	H$\cdots$He	0.00 114	-0.00 09	-0.00 09	0.00 677	-0.00 124	6.66e -12
$GeH_4\cdots Ne$	H$\cdots$Ne	0.00 261	-0.00 225	-0.00 225	0.01 583	-0.00 283	7.86e -12
$GeH_4\cdots Ar$	H$\cdots$Ar	0.00 394	-0.00 286	-0.00 286	0.01 970	-0.00 349	9.22e -12
$GeH_4\cdots Kr$	H$\cdots$ Kr	0.00 530	-0.00 386	-0.00 386	0.02 493	-0.00 430	4.53e -12

The topological properties of the scalar field electron density ($ñ(r)$) can be described by the numbers and the categories of the critical points. A critical point is the spatial position where the first derivative of the $\rho(r)$ is zero, namely as following:

$$\nabla\rho(r) = i\frac{\partial}{\partial x}\rho(r) + j\frac{\partial}{\partial y}\rho(r) + k\frac{\partial}{\partial z}\rho(r) = 0$$

According to the critical point's curvature obtained by calculating the second derivative of the $\rho(r)$, the type of the critical point can be defined. The Hessian matrix of electron density is composed by nine secondary de-
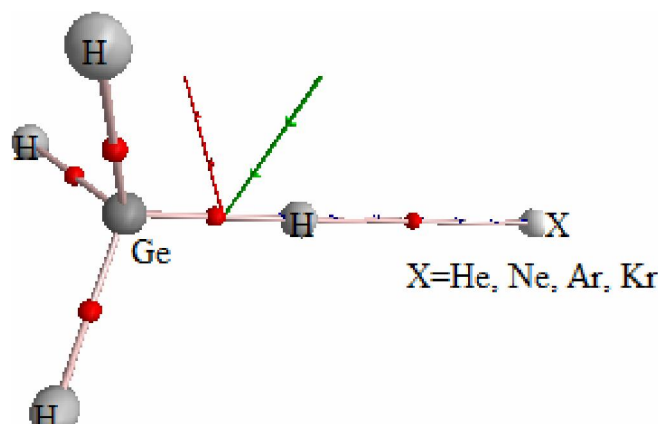
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Figure 4 : The molecular graph of GeH₄•••Y(Y=He, Ne, Ar, Kr)

rivatives of ρ(r) in three dimensions. The three eigenvalues (λ_1, λ_2 and λ_3) can be acquired by performing a diagonalized operator on Hessian matrix. The sum of the three eigenvalues is equal to Laplacian of the electron density ($\nabla^2\rho(r) = \lambda_1 + \lambda_2 + \lambda_3$). Among the three eigenvalues, if two of them are negative and the other is positive, the corresponding critical point is designated as the bond critical point (BCP) and marked as (3, -1), indicating the linkage between the two atoms. The electron density topological properties of a molecule depend on electron density gradient vector field and $\nabla^2\rho(r)$. In general, the electron density of a BCP ($\rho(r_c)$) is related to the strength of the bond: the larger the $\rho(r_c)$ is, the stronger the bond will be; the smaller the $\rho(r_c)$ is, the weaker the bond will be. The $\nabla^2\rho(r)$ of a BCP reflects the characteristic of the bond. If $\nabla^2\rho(r_c)<0$, BCP charges will be concentrated, and the more negative $\nabla^2\rho(r_c)$ is, the more covalent property will be; if $\nabla^2\rho(r_c)>0$, BCP charges will be dispersed, and the more positive $\nabla^2\rho(r_c)$ is, the more ionic property will be.

The electron density topological properties of the H1···Y(Y=He, Ne, Ar, Kr) critical points in the complexes are listed in TABLE 6. The three eigenvalues of the electron density Hessian matrix of H1···Y are all "one positive and two negative". Therefore, the critical points between the atom pair of H1···Y belong to the type of BCPs, and H1···Y has a certain degree of bond property. Further, molecular graph is the intuitionistic expression of the electron density topological property, and it can reliably describe the bond structures. Figure 4 is the molecular graphs of the GeH₄…Y(Y=He, Ne, Ar, Kr) complexes, it also shows that there are a bond critical points (red points between H and Y) between

H1 and Y atom pair, which suggests bond behavior between corresponding two atoms. The $\rho(r)$ of H1···Y in the four complexes are on the small scale of 0.00114 ~ 0.00530 a.u.. This indicates that the interactions in the four complexes are weak, which is in good agreement with the interaction energy analysis and NBO analysis. In addition, the $\nabla^2\rho(r)$ of the corresponding critical points are all small negative values (-0.00430 ~ -0.00124 a.u.). This shows that there is concentration the electron density within the H1···Y atoms pair region, and this kind of interaction is with non-electrostatic property but covalent character, which is agreed well with the NBO analysis. The ellipticity ε is defined as λ_1/λ_2-1, of which the λ_1 and λ_2 are the two eigenvalues of the Hessian matrix of electron density. The ellipticity provides a measure for the σ or π character of a bond. In general, the less the ε is, the stronger the σ character is; contrariwise, the π character is. As shown in TABLE 6, all the ellipticity ε of H1···Y weak bonds are close to zero, this indicates that H1···Y weak bonds have much σ character.

CONCLUSIONS

MP2/aug-cc-pvtz level was used to optimize geometries of the four complexes between GeH₄ and Y(Y=He, Ne, Ar, Kr) have been calculated at the. Reported the structures and electronic properties of the GeH₄…Y(Y=Ar, Kr) intermolecular interactions. The calculated interaction energies with basis set super-position error (BSSE) correction revealed that the relative stabilities of the complexes in the order: GeH₄…He < GeH₄…Ne < GeH₄…Ar ≈ GeH₄…Kr. The calculated results showed that the interactions between GeH₄ and Y(Y=He, Ne) belong to van der Waals force, and those between GeH₄ and Y(Y=Ar, Kr) belong to weak hydrogen bond. Electron behavior and electron density topological analysis showed that GeH₄…Y(Y=Ar, Kr) hydrogen bond is with a non-electrostatic property.

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