Vol 16 No 8, August 2007
1009-1963/2007/16(08)/2394-06
Chinese Physics
© 2007 Chin. Phys. Soc.
and IOP Publishing Ltd

DFT study on the structure and spectra of Ga_5P_5 cluster*

Zhang Cai-Rong(张材荣)[a)b)c)], Chen Hong-Shan(陈宏善)[a)†],
Song Yan(宋 燕)[a)], and Xu Guang-Ji(许广济)[c)]

[a)] *College of Physics and Electronic Engineering, Northwest Normal University, Lanzhou* 730070, *China*
[b)] *School of Science, Lanzhou University of Technology, Lanzhou* 730050, *China*
[c)] *State Key Laboratory of Nonferrous Metal Materials, Lanzhou University of Technology, Lanzhou* 730050, *China*

(Received 8 February 2006; revised manuscript received 29 December 2006)

In this paper, possible structures of Ga_5P_5 cluster were optimized by using density functional method with generalized gradient correction (B3LYP). The electronic structure of the isomers with lower energy was studied. The most stable structure obtained for Ga_5P_5 is a distorted pentaprism. The Ga-P bond formed in the cluster is strongly ionic. Based on NBO analysis, an average value of 0.59 electron transfers from Gallium to Phosphorus. The bond length 2.33–2.43 Å is around the value in bulk GaP. The HOMO-LUMO gap is about 2.2 eV. The dipole moment and polarizability are calculated, and the IR and Raman spectra are also presented.

Keywords: Ga_5P_5 cluster, density functional theory, electronic structure, IR and raman spectra
PACC: 3640, 7115M

1. Introduction

The chemical and physical properties of a cluster are different from the properties of the component atoms/molecules or of the extended bulk material. The size dependent evolution of the structure and properties of clusters is an extremely active area of research due to their importance in both fundamental science and applied technology. Existing experimental methods can hardly determine the structure of clusters directly. Theoretical calculation, comparing with experimental values of the physical and optical properties, is the most common way to obtain structural information of clusters. *Ab initio* methods, however, face great difficulty when applied to mixed clusters as the number of isomers of a cluster increase exponentially with the size. GaP shows special electronic and optical properties and is a promising material for photoelectric industry,[1−3] but the study of GaP cluster is still limited. Experimentally, Taylor *et al*[4] studied the photoelectronic spectra of the anions of Ga_xP_y cluster up to 18 atoms. Li *et al*[5] measured the IR spectra of GaP, Ga_2P and GaP_2. Theoretically, Feng and Balasubramanian optimized the structure and calculated the ionization energy of Ga_mP_n $(m+n \leq 5)$ clusters by using CASSCF (complete active space self-consistent field) followed by MRSDCI (multi-reference single and double excited configuration interaction).[6] Jia and Wu Haishun also studied the structure and ionization energy of the Ga_mP_n $(m+n \leq 5)$ by using B3LYP method.[7] Starting from the initial structure based on Si_{2n} and Ge_{2n}, Andreoni[8] investigated the structures of Ga_nAs_n, Al_nAs_n, and Ga_nP_n $(n \leq 5)$ by using ab initio method. Our group studied the geometric and electronic structures of Ga_nP_n $(n \leq 4)$ clusters.[9] In this paper, we intend to study the structure and spectra of Ga_5P_5 cluster.

2. Method

Referencing the stable isomers of Ga_nAs_n,[10] Cd_nSe_n and Cd_nS_n,[11,12] and based on the structure character of Ga_nP_n $(n = 1-4)$,[9] we designed over 40 possible structures for Ga_5P_5. These structures were optimized by using standard density functional theory (DFT) method without any constraint. The density functional adopted is Beck's three parameter gradient corrected exchange potential with the Lee-Yang-Parr's gradient corrected correlation potential.[13−15] The geometry optimization was performed at the basis level of LanL2DZ. For the isomers of lower energy, the structure was further optimized by using basis

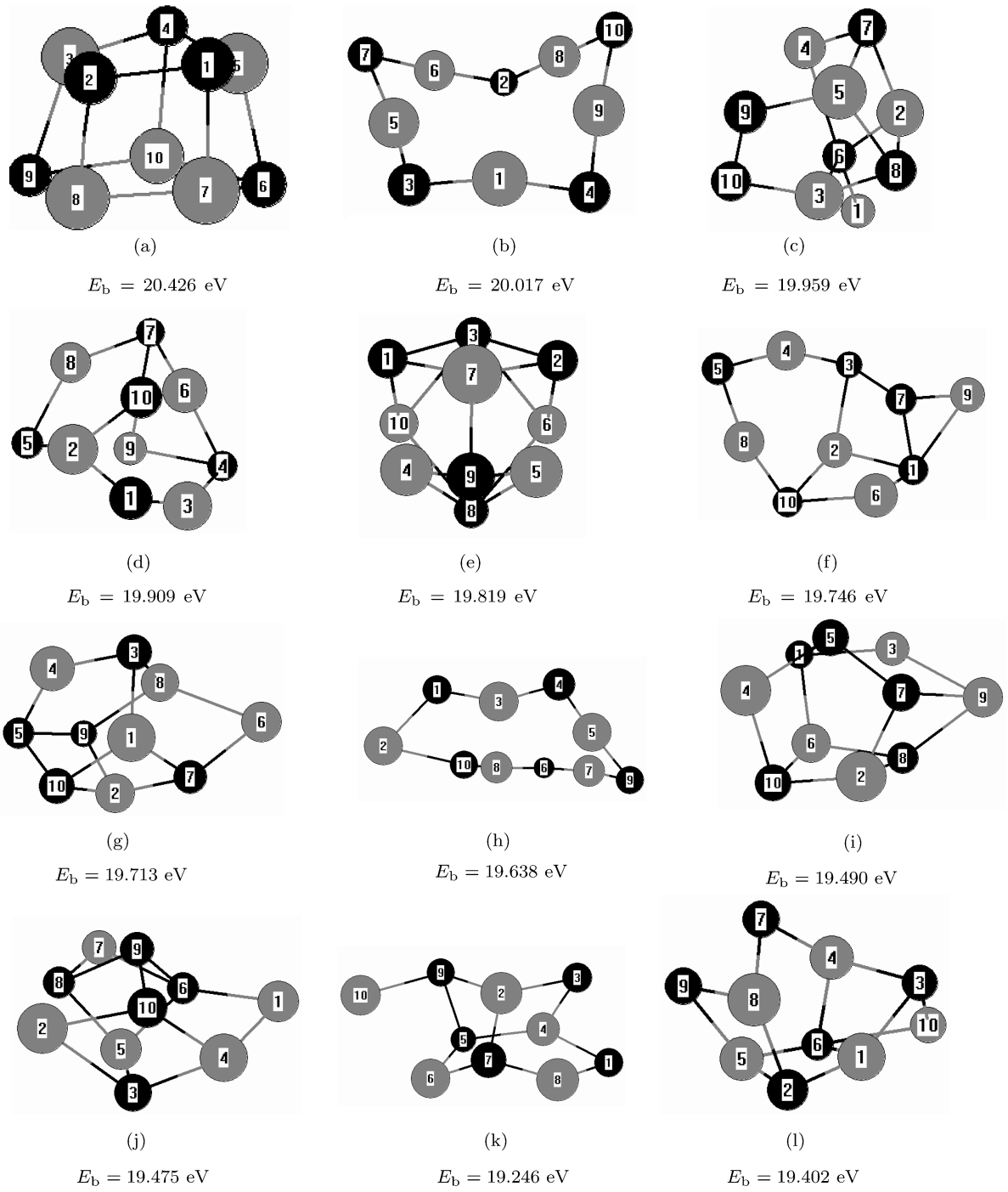
*Project supported by the National Natural Science Foundation of China (Grant No 10647006) and Natural Science Foundation of Gansu Province, China (Grant No 3ZS042-B25-023).
†Corresponding author: E-mail: chenhs@nwnu.edu.cn (Chen Hong-shan), zhcrxy@lut.cn (Zhang Cai-Rong)

6-31+G*. The electronic properties and the spectra were calculated at the latter basis level.

3. Results and Discussions

3.1. Structures of Ga_5P_5 cluster

After geometry optimization, some structures changed dramatically, and some optimizations from different initial isomers lead to same structure. The 12 isomers with lower energy are illustrated in Fig.1. Vibrational analysis gives no imaginary frequency, which shows that the structures are located at the minima of the potential surface.



(a) E_b = 20.426 eV; (b) E_b = 20.017 eV; (c) E_b = 19.959 eV; (d) E_b = 19.909 eV; (e) E_b = 19.819 eV; (f) E_b = 19.746 eV; (g) E_b = 19.713 eV; (h) E_b = 19.638 eV; (i) E_b = 19.490 eV; (j) E_b = 19.475 eV; (k) E_b = 19.246 eV; (l) E_b = 19.402 eV

Fig.1. Optimized structures and the total binding energy of stable isomers of Ga_5P_5 cluster. (●-Pa; ●-P).

The most stable isomer of Ga_5P_5 (structure a in Fig.1) is similar to that of Ga_5As_5,[16] which is a pentaprism with heavily distorted side quadrangles. The P–Ga–P angles are larger than 100°, but the Ga–P–Ga angles are generally smaller than 80°. This implies that the P–Ga bond formed is typically covalent, and it can be explained by the reason that P atom has five valence electrons and can form hybrid orbital more flexibly than Ga atom. There are one P–P bond and one Ga–Ga bond, which give the shortest and longest bond length respectively. The P–Ga bond length ranges from 2.33 Å to 2.43 Å, which is close to the P–Ga distance (2.36 Å) in bulk GaP.

Isomer (b) is a wing structure. The Ga–P–Ga angles are about 90 ? and the P–Ga–P angles are close to 180°. The bond length in this structure is from 2.26Å to 2.28Å. Isomer (c) is composed of one pentagon and three quadrangles. Isomer (d) is a cap-like structure. Isomer (e) is built up from rhombus. Isomer (f) has one Ga_3P_3 hexagon and two distorted quadrangles. Isomer (g) is formed by three pentagons and two quadrangles. Isomer (h) is a contorted decagon structure. Isomer (i) is constructed by two pentagons and five distorted quadrangles.

Table 1. The bond lengths (Å) and bond angles (degree) optimized by using B3LYP/6-31+G* for the most stable isomer of Ga_5P_5 cluster.

Definition	value	definition	value	definition	value
P1–P2	2.247	Ga7–Ga8	2.479	P2–Ga3	2.346
Ga3–P4	2.329	P4–Ga5	2.352	P1–Ga5	2.407
P6–Ga7	2.412	Ga8–P9	2.331	P9–Ga10	2.418
P6–Ga10	2.326	Ga5–P6	2.355	P1–Ga7	2.424
P2–Ga8	2.411	Ga3–P9	2.432	P4–Ga10	2.388
Ga3–P4–Ga5	83.95	Ga5–P6–Ga10	74.15	Ga5–P6–Ga7	74.59
Ga3–P2–Ga8	75.62	Ga5–P1–Ga7	73.44	Ga7–P6–Ga10	93.47
Ga3–P9–Ga8	75.49	Ga5–P4–Ga10	73.05	Ga8–P9–Ga10	79.89
P2–P1–Ga5	90.48	P1–P2–Ga3	110.46	P1–P2–Ga8	106.19
P1–Ga7–P6	103.33	P1–Ga5–P4	129.29	P2–Ga3–P4	120.11
P4–Ga3–P9	104.90	P1–Ga5–P6	105.62	P2–Ga3–P9	102.31
P4–Ga10–P9	103.56	P4–Ga10–P6	101.06	P2–Ga8–P9	103.44
P6–Ga10–P9	134.77	P2–P1–Ga7	79.35	P1–Ga7–Ga8	98.9
P6–Ga7–Ga8	99.80	P2–Ga8–Ga7	75.23	Ga7–Ga8–P9	127.74

Natural Bond Orbital (NBO) analysis[17] was applied to calculate the charge population. For the most stable isomer of Ga_5P_5, the charges on P1, P2, P4, P6, P9 and Ga3, Ga5, Ga7, Ga8, Ga10 atoms are −0.389, −0.504, −0.665, −0.713, −0.682, 0.627, 0.662, 0.477, 0.520, 0.667 electrons respectively. An average value of 0.591 electrons transfers from Gallium to Phosphorus. It suggests that the covalent bond formed in Ga_5P_5 cluster is strong ionic.

The HOMO–LUMO gaps for the isomers (a)–(f) in Fig.1 are 2.166 eV, 2.811 eV, 2.278 eV, 2.601 eV, 2.341 eV, 2.297 eV respectively. The energy gap is sometimes regarded as a measure of the stability of clusters.[18] For Ga_5P_5 cluster, the most stable structure judged by binding energy is isomer (a), but isomer (b) has largest energy gap.

The valence electronic density of states (DOS) for isomers (a) and (b) are plotted in Fig.2. The levels are represented by Gaussian distributions with a half width of 0.05 eV. The alternate arrangement of Ga and P atoms in isomer (b) ensures that each conjoint pair of GaP atoms has 8 electrons, and the regular bond angles in the ring structure match well with the hybrid orbitals of Ga and P atoms. Such a structure makes the DOS of isomer (b) show obviously a 'band' feature, and it results in a large energy gap.

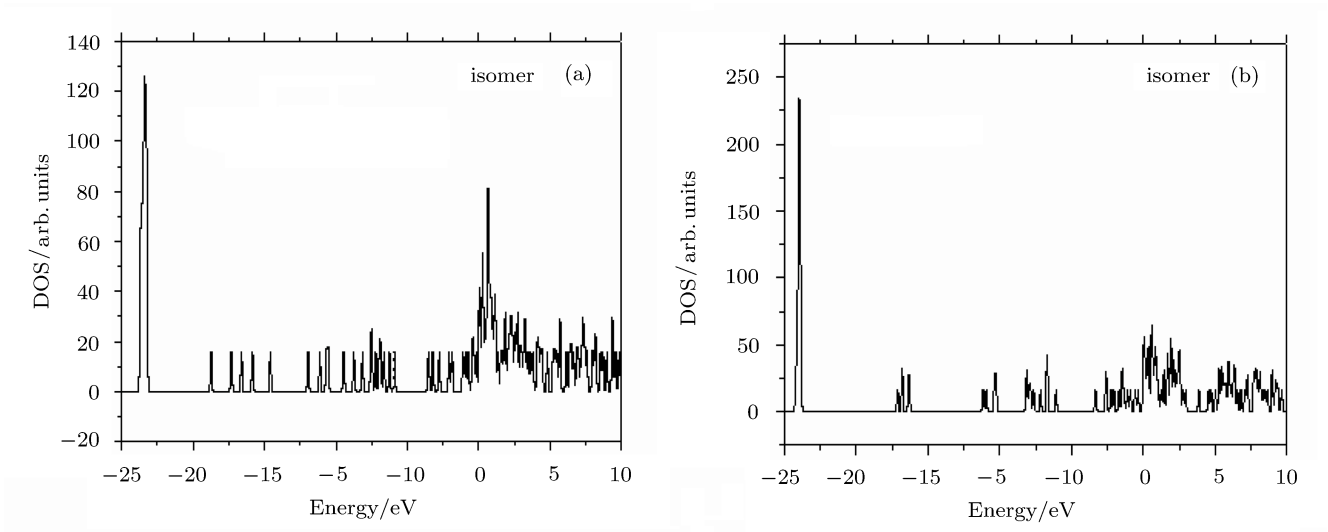


Fig.2. Valence electronic density of states for the most stable isomer (a) and isomer (b) of Ga_5P_5 cluster calculated by using B3LYP/6-31+G*.

3.2. Polarizabilities and hyperpolarizabilities of Ga_5P_5 cluster

The dipole moments, polarizability and hyperpolarizability are important properties of clusters. They decide the short range intermolecular forces, the long range induction and dispersion interactions. The strength of these interactions then determines the cross section of different scattering and collision processes. Table 2 lists the values of the dipole moments, polarizabilities and first hyperpolarizabilities of Ga_5P_5 cluster. In addition to the individual tensor components, we also calculated the isotropic polarizability, the polarizability anisotropy invariant and the average hyperpolarizability, which are defined as Ref.[19]:

$$\alpha = \frac{1}{3}(\alpha_{XX} + \alpha_{YY} + \alpha_{ZZ}),$$

$$\Delta\alpha = \Big[\frac{(\alpha_{XX} - \alpha_{YY})^2 + (\alpha_{YY} - \alpha_{ZZ})^2 + (\alpha_{ZZ} - \alpha_{XX})^2}{2}\Big]^{1/2},$$

$$\beta_{||} = \frac{1}{5}\sum_i(\beta_{iiZ} + \beta_{iZi} + \beta_{Zii}).$$

The isotropic polarizability, polarizability anisotropy invariant and hyperpolarizability are $\alpha = 277.39$, $\Delta\alpha = 38.23$ and $\beta_{||} = 135.75$ respectively. All the values are given in atomic unit.

Table 2. The dipole moment, polarizability and hyperpolarizability of the most stable Ga_5P_5 calculated at B3LYP/6-31+G* (in a.u.).

Dipole	X	Y	Z			
	0.179	−0.334	−0.241			
Polarizability	XX	YY	ZZ	XY	XZ	YZ
	299.69	276.94	255.55	0.71	3.02	−0.32
Hyperpolarizability	XXX	XXY	XXZ	XYY	XYZ	
	−134.33	−99.16	−80.00	−27.42	−42.65	
	YYY	YYZ	XZZ	YZZ	ZZZ	
	−51.22	−124.66	−11.58	19.34	−30.59	

3.3. IR and Raman spectra of Ga_5P_5 cluster

There are 24 vibration modes from 84.83 cm^{-1} to 413.77 cm^{-1} for the most stable Ga_5P_5 cluster. Table 3 lists the frequencies, the IR intensities and Raman activities. Figure 3 shows the calculated IR and Raman spectra. The vibration of the strongest IR and Raman mode V23, V22, V21, V19 and V10 are illustrated in Fig.4, which shows the displacement of atoms and the dipole derivative unit vector. Mode V23 at 369.34 cm^{-1} is a stretch movement mainly due to P4 and the Ga atoms bonded to it. Mode V22 at 365.48 cm^{-1} is a swing movement mainly of P6 and P9 atoms in the underside. The large displacement of the light P atoms in the same direction in these two modes results in large change of the dipole moment and strong IR intensity. Modes V21 and V19 are the breathing vibration of the underside (P6–Ga7–Ga8–P9–Ga10) and upside (P1–P2–Ga3–P4–Ga5) respectively. These two modes give the strongest Raman activity and strong IR intensity as well. Mode V10 is the breathing vibration of the whole cluster, P and Ga atoms move in opposite directions. This mode is the third strongest Raman vibration but is IR inactive.

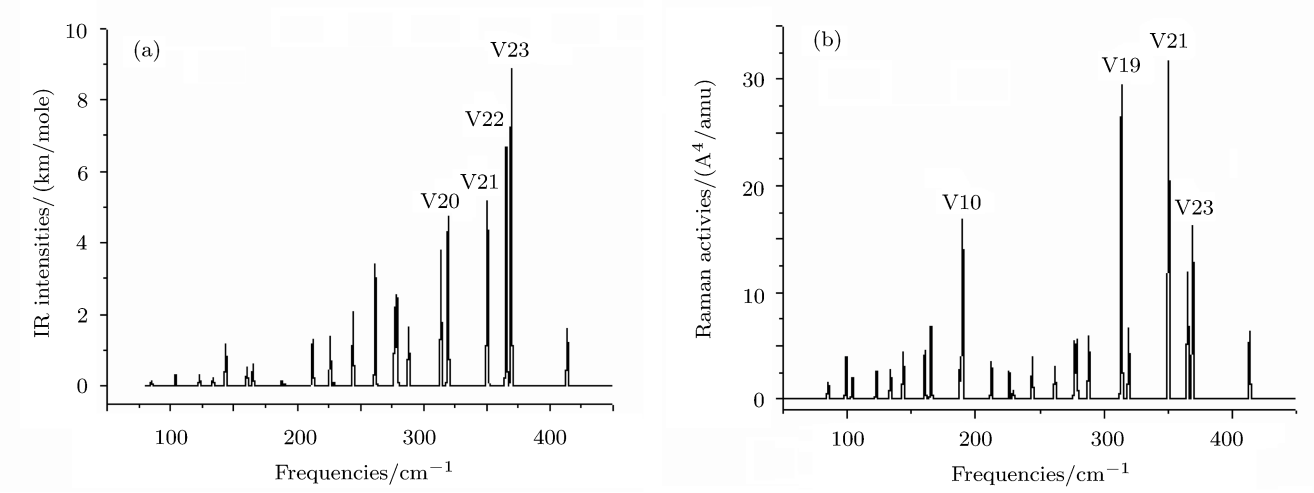


Fig.3. IR and Raman spectra of the most stable isomer of Ga_5P_5 calculated at B3LYP/6-31+G*.

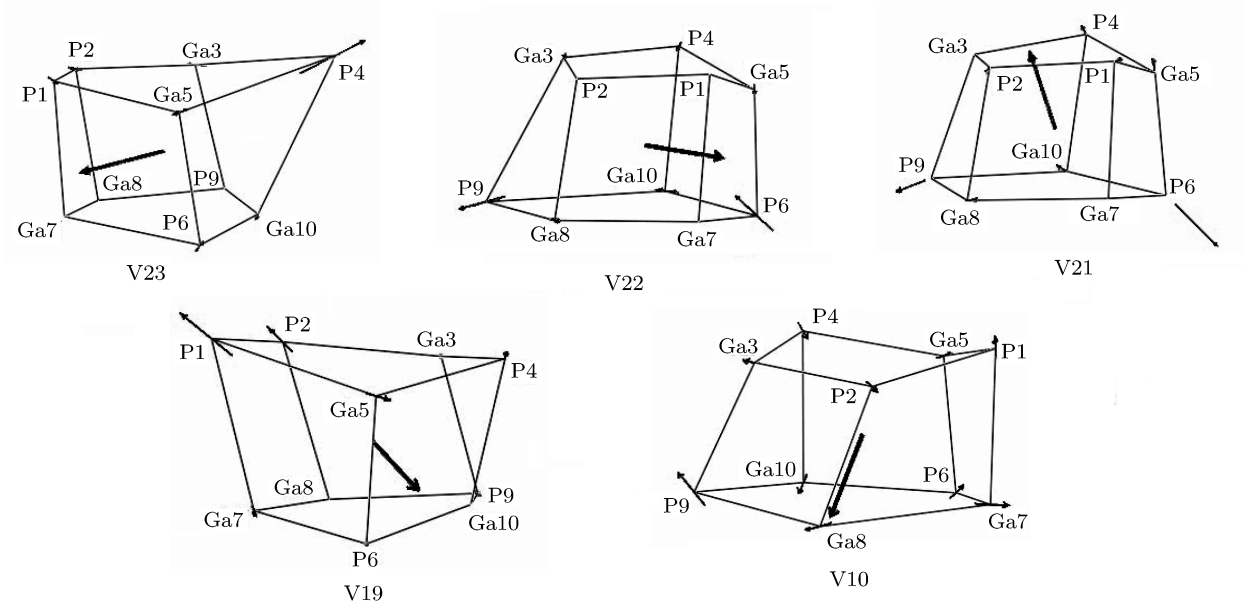


Fig.4. Vibration modes V23, V22, V21, V19, V10 of Ga_5P_5 cluster. The displacement of the atoms and dipole derivative unit vector are showed.

Table 3. Vibrational frequencies, IR intensity and Raman activity of the most stable Ga_5P_5 cluster calculated by B3LYP/6-31+G*.

Vibrational mode	Frequency /cm^{-1}	IR intensity /(km/mol)	Raman active /(Å^4/amu)	Vibrational mode	Frequency /cm^{-1}	IR intensity /(km/mol)	Raman active /(Å^4/amu)
V1	84.83	0.160	2.019	V13	229.29	0.094	1.088
V2	98.86	0.002	5.021	V14	244.19	2.579	4.979
V3	103.77	0.379	2.563	V15	261.79	4.269	3.746
V4	122.66	0.385	3.316	V16	277.24	2.736	6.845
V5	133.43	0.274	3.414	V17	278.96	3.197	7.026
V6	143.44	1.485	5.560	V18	288.24	2.037	7.440
V7	160.28	0.652	5.676	V19	313.75	4.738	36.85
V8	165.04	0.787	8.566	V20	319.41	5.920	8.259
V9	187.70	0.178	3.769	V21	350.50	6.484	39.71
V10	189.69	0.076	21.15	V22	365.48	8.354	14.84
V11	212.27	1.616	4.360	V23	369.34	11.14	20.41
V12	226.17	1.755	3.227	V24	413.77	2.029	8.050

4. Conclusion

Possible structures of Ga_5P_5 cluster are optimized by using DFT/B3LYP method. The most stable isomer obtained is a distorted pentaprism. The Ga-P bond formed in the cluster is typically covalent but has strong ionicity. The bond lengths (2.33–2.43Å) are around the value (2.36Å) in bulk GaP. The HOMO-LUMO gap of Ga_5P_5 is about 2.2 eV. The polarizabilities and first hyperpolarizabilities are calculated. The isotropic polarizability is α= 277.39 (a.u.) and the average hyperpolarizability is $\beta_{||}$=135.75 (a.u.). Vibrational analysis shows that the strongest IR lines are at 369.34 cm^{-1} and the strongest Raman shifts are 350.50 cm^{-1}.

References

[1] Kang D, Ko J H, Bae E, Hyun J and Park W 2004 *J. Appl. Phys.* **96** 7574

[2] Liu B D, Bando Y, Tang C C, Golberg D, Xie R G and Sekiguchi T 2005 *Appl. Phys. Lett.* **86** 083107

[3] Rivas J G, Lagendijk A, Tjerkstra R W, Vanmaekelbergh D and Kelly J J 2002 *Appl. Phys. Lett.* **80** 4498

[4] Taylor T R, Asmis K R and Xu C S 1998 *Chem. Phys. Lett.* **297** 133

[5] Li S, Van Zee R J and Weltner W 1993 *J. Phys. Chem.* **97** 11393

[6] Feng P Y and Balasubramanian K 1998 *Chem. Phys. Lett.* **288** 1

[7] Jia W H and Wu H S 2004 *Acta Phys. Sin.* **53** 1056 (in Chinese)

[8] Andreoni W 1992 *Phys. Rev.* B **45** 4203

[9] Zhang C R, Chen H S and Wang G H 2004 *Chem. Res. Chin. U.* **20** 640

[10] Song K M, Ray A K and Khowash P K 1994 *J. Phys.* B: *At. Mol. Opt. Phys.* **27** 1637

[11] Deglmann P, Ahlrichs R and Tsereteli K 2002 *J. Chem. Phys.* **116** 1585

[12] Zheng H P and Hao J 2005 *Chin. Phys.* **14** 529

[13] Becke A D 1993 *J. Chem. Phys.* **98** 5648

[14] Miehlich B, Savin A and Stoll H 1989 *Chem. Phys. Lett.* **157** 200

[15] Lee C, Yang W and Parr R G 1988 *Phys. Rev.* B **37** 785

[16] Yi J Y 2000 *Chem. Phys. Lett.* **325** 269

[17] Carpenter J E and Weinhold F 1988 *J. Mol. Struct.* (Theochem) **41** 169

[18] Zope R R, Blundell S A and Guet C 2001 *Phys. Rev.* A **63** 043202

[19] Sun Y L, Chen X S and Sun L Z 2003 *Chem. Phys. Lett.* **381** 397