

Bond population analysis on combination of favorable growth unit of $\text{Al}(\text{OH})_3$ crystals

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Abstract: The quantum chemical calculation on four representative combination modes of the favorable growth unit $\text{Al}_6(\text{OH})_{18}(\text{H}_2\text{O})_6$ of $\text{Al}(\text{OH})_3$ crystals and the single unit were calculated. On the base of the prior investigation, and from the point of view of bond population and net atomic charge, the relationships between the combination mode of the favorable growth unit and the relative intensity of chemical bond of the systems were discussed. The quantum chemistry calculations were performed at RB3LYP/6-31G and RHF/6-31G levels by ab initio and DFT methods respectively. From the point of view of bond population, it can be preliminarily presumed that the interatomic bond force of the system with side-face-combination-B mode is weaker to a certain extent. From the point of view of the net charge, when the combination mode is obverse-face-combination-D, the interatomic bond force will be enhanced.

Key words: gibbsite; growth unit; combination; bond population; atomic net charge

1 Introduction

It is well known that there are many technical puzzles on how to enhance the strength of alumina in the domestic production of alumina. From the actual research it has been indicated that the strength of alumina is mainly related to the strength of $\text{Al}(\text{OH})_3$ precipitated from sodium aluminate solution[1–9].

LI et al[10–17] studied in-depth the structural characteristics of supersaturated sodium aluminate solution and growth units of $\text{Al}(\text{OH})_3$. They brought forward and proved that $\text{Al}_6(\text{OH})_{18}(\text{H}_2\text{O})_6$ with hexagon face shape was the favorable growth unit of gibbsite. For the sake of gaining alumina with high strength, the combination mode of growth units of $\text{Al}(\text{OH})_3$ must be controlled.

On the base of the investigation by LI et al[10–17], the quantum chemistry calculation on the favorable growth unit of gibbsite has been performed[18–21]. In Refs.[18–20], the total energy, orbital population and atomic charge of $\text{Al}_6(\text{OH})_{18}(\text{H}_2\text{O})_6$ were calculated using Dipole & Sphere solvent model at 6-31G, B3LYP/6-31G, 6-31G*, B3LYP/6-31G*, 6-31G**, B3LYP/6-31G** levels. The bonding orientation of $\text{Al}_6(\text{OH})_{18}(\text{H}_2\text{O})_6$

was analyzed. In Ref.[21], the dipole moment, total energy, orbital population and orbital energy of four representative combination modes of the favorable growth unit $\text{Al}_6(\text{OH})_{18}(\text{H}_2\text{O})_6$ of $\text{Al}(\text{OH})_3$ crystals precipitating were calculated by ab initio at RHF/STO-3G, RHF/3-21G, RHF/6-31G levels and DFT at RB3LYP/STO-3G, RB3LYP/3-21G, RB3LYP/6-31G levels with Dipole & Sphere solvent model. The effect of various combination models on Van der Waals force was analyzed using dipole moment and molecular radius. The effect of various combination models on chemical bond force was analyzed using total energy, orbital population and orbital energy. All calculation results indicated that the bridge OH group is easier to bond, and the favorable bonding orientation is located at the bridge OH group orientation, and the obverse-face combination mode is the strongest and firmest, this combination mode is probably more possible than the others.

In this paper, on the base of the above studies, and from the point of view of bond population and net atomic charge, the relationship between the combination mode of the favorable growth unit and the relative intensity of chemical bond of the systems was discussed. The effect on the transfer relation of inter-atomic electrons will also be approached, for looking forward

to gaining the microscopic combination image of the favorable growth unit.

2 Calculation models and theories

2.1 Calculation models

The figure of favorable growth unit $\text{Al}_6(\text{OH})_{18}(\text{H}_2\text{O})_6$ is hexagon of face shape. Four kinds of typical combination modes of the favorable growth unit were designed. Regarding six Al as structure framework, there are four modes: side-uprightness-combination-A, side-face-combination-B, obverse-uprightness-combination-C and obverse-face-combination-D respectively. Fig.1 shows the calculation models of four typical combination modes. In Fig.1, unit 1 and unit 2 are two favorable growth units which come in on the combination. The calculation model of single growth unit $\text{Al}_6(\text{OH})_{18}(\text{H}_2\text{O})_6$ is shown in Fig.2.

2.2 Calculation theory and method

Mulliken population analysis is a theoretic method which can give some concise information of the electronics distribution in atomics, molecules and chemical bonds, according to SCF calculation results of MO wave functions.

In this paper, the total gross population and the net charge on every atom of the studied systems will be calculated, and from the point of view of whole average of calculation results the effect of the combination modes will be studied.

Based on ab initio Self Consistent Field molecular orbital theory and Density Function Theory method, the total gross population and the net charge were

calculated at 6-31G levels with Dipole & Sphere solvent model. The Density Function Theory method adopted B3LYP Becke model with three parameters. The calculations were performed at C2 workstation in Central South University by Gaussian98 program. Based on the Molecular Mechanics Force Field, the geometric optimization was implemented by MM+ method using conjugation gradient Polak-Ribiere algorithm and the terminal condition was RMS gradient of 0.42 kJ/mol or maximum cycles of 1 800 times.

3 Results and discussion

3.1 Analysis of bonding population

The average values of gross population of atoms in the systems of four typical combination modes and single unit were calculated at RB3LYP/6-31G and RHF/6-31G levels. According to the calculation results, the average values of total gross population of aluminum, terminal oxygen and bridge oxygen in four typical combination modes and single unit were calculated. Figs.3 and 4 show the results calculated at RB3LYP/6-31G and RHF/6-31G levels respectively. In addition, the calculation results of total energy of four typical combination modes are given in Table 1.

It can be seen from Fig.3 that, there is some difference on average values of the gross population between the four kinds of atoms in two combination units and those atoms in single unit.

As compared with the single unit, there is a remarkable change in the average values of the gross

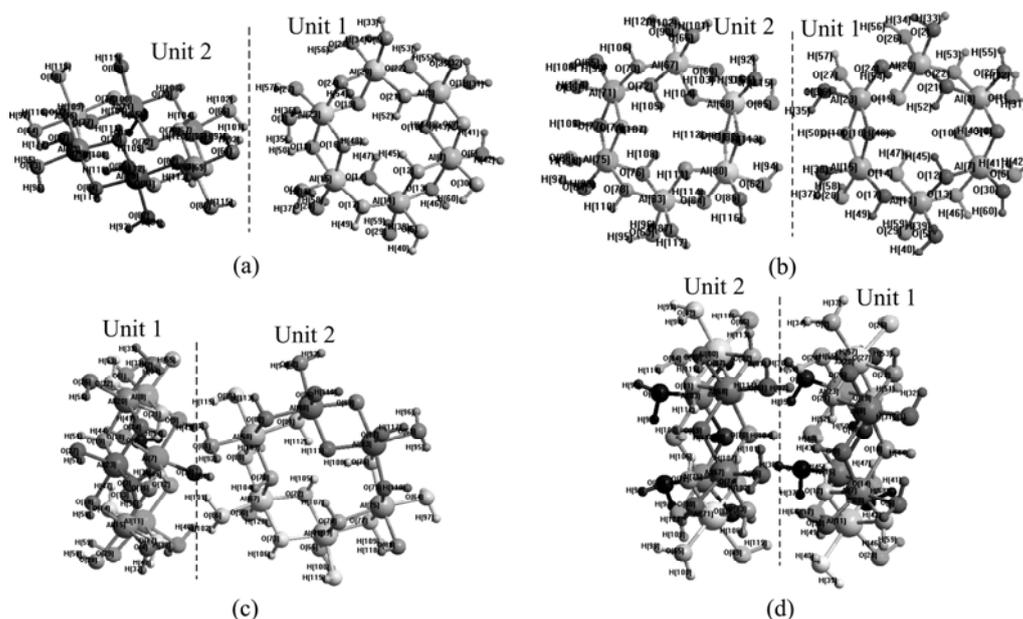


Fig.1 Calculation models of four combination modes of $\text{Al}_6(\text{OH})_{18}(\text{H}_2\text{O})_6$: (a) Side-uprightness-combination-A; (b) Side-face-combination-B; (c) Obverse-uprightness-combination-C; (d) Obverse-face-combination-D

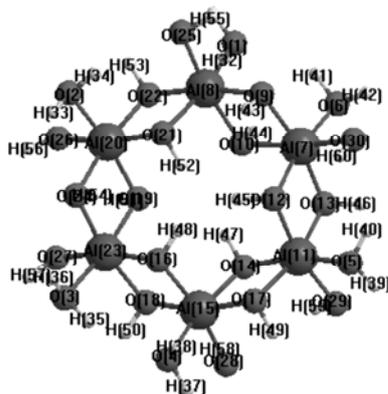


Fig.2 Calculation model of $\text{Al}_6(\text{OH})_{18}(\text{H}_2\text{O})_6$

population of four typical atoms in the system with side-face-combination-B mode, whereas the change is on the small side with side-uprightness-combination-

A mode. The average values of gross population of the bridge oxygen are decreased in the systems with obverse-uprightness-combination-C and obverse-face-combination-D modes, and that the changes of the average values of gross population of the terminal oxygen in these two systems are small.

The average values of gross population of aluminum atoms in the systems with side-face-combination-B, obverse-uprightness-combination-C and obverse-face-combination-D modes are decreased. These calculation results may be presumed that after combination, the action force between aluminum and atoms around is lessened. But this changing trend is not totally the same in Unit 1 and Unit 2 of the system, especially in obverse-face-combination-D system.

The average value of gross population of terminal oxygen in the system with side-face-combi-

Table 1 Calculation results of total energy

Calculation method	Total energy/(kJ · mol ⁻¹)			
	A	B	C	D
RHF/6-31G	-17 161 870.709 2	-17 161 675.775 7	-17 161 952.862 2	-17 162 149.812 7
RB3LYP/6-31G	-17 227 304.713 4	-17 227 399.004 1	-17 227 403.614 7	-17 227 576.266 0

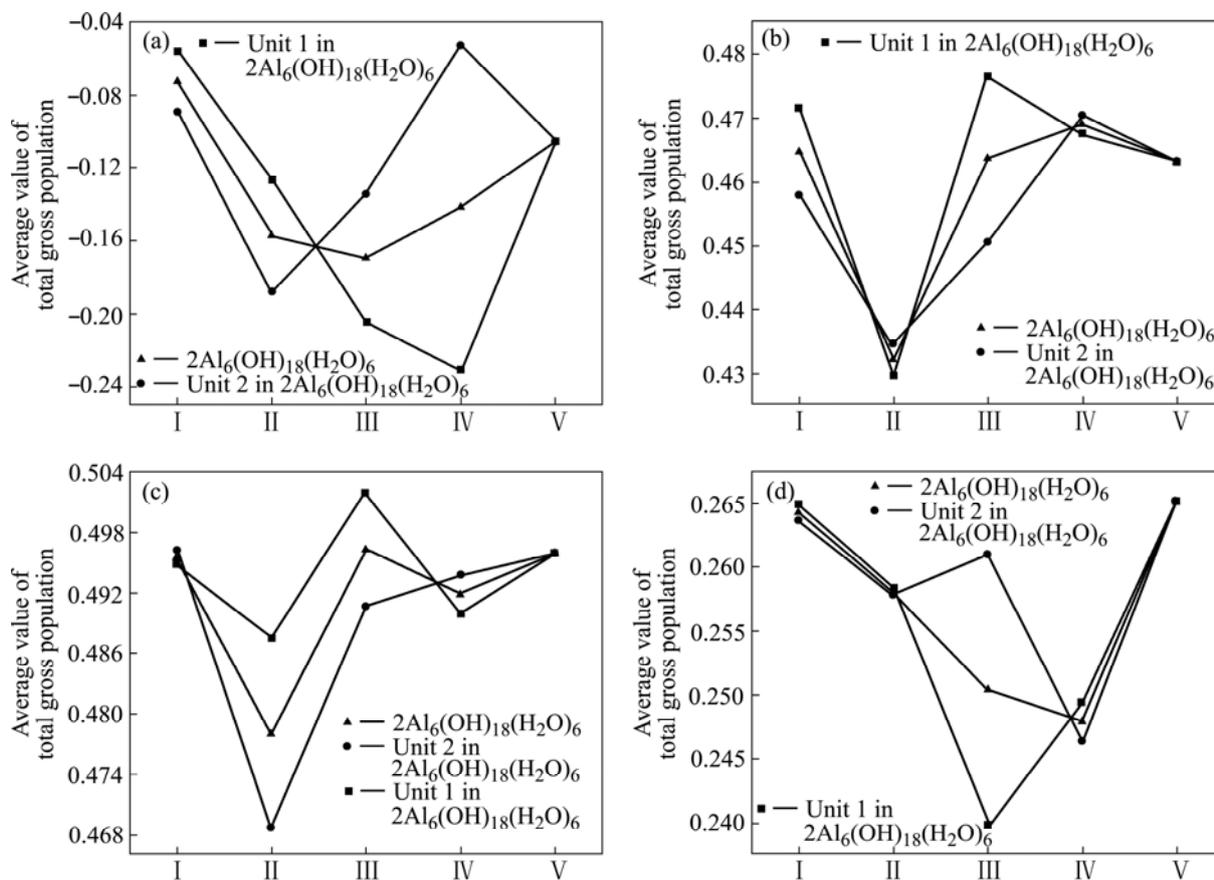


Fig.3 Average value of total gross population on Al(a), terminal oxygen in Al-H₂O (b), terminal oxygen in Al-OH (c) and bridge oxygen(d) of systems calculated at RB3LYP/6-31G level (I represents combination-A; II represents combination-B; III represents combination-C; IV represents combination-D; V represents single growth unit)

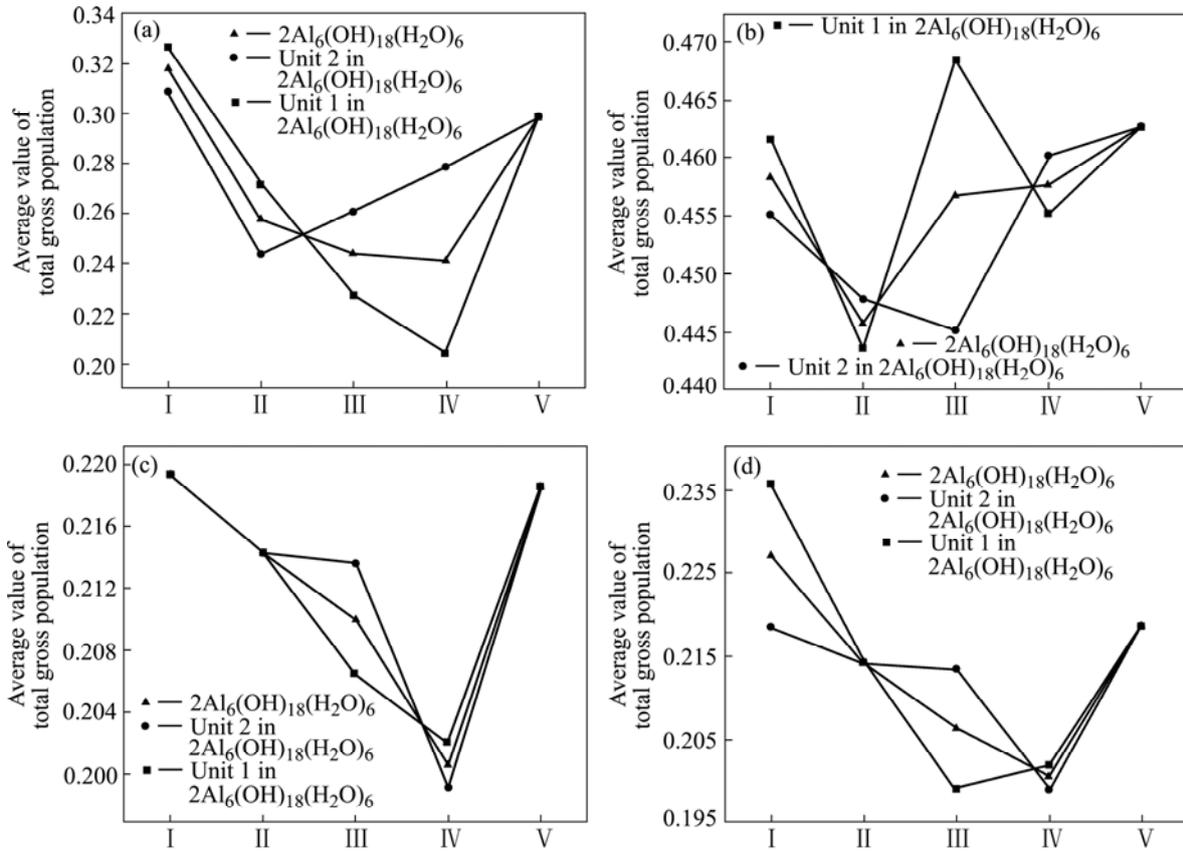


Fig.4 Average value of total gross population on Al(a), terminal oxygen in Al-H₂O (b), terminal oxygen in Al-OH (c) and bridge oxygen(d) of systems calculated at RHF/6-31G level(I represents combination-A; II represents combination-B; III represents combination-C; IV represents combination-D; V represents single growth unit)

nation-B mode is the lowest, whereas the change of the other three kinds of combination modes is not distinct. At the same time, the difference in average values of gross population of terminal oxygen (in Al-H₂O) in Unit 1 and Unit 2 of the system with obverse-uprightness-combination-C mode is relatively bigger, and the difference in average values of gross population of terminal oxygen (in Al-OH) in Unit 1 and Unit 2 of the systems with side-face-combination-B and obverse-uprightness-combination-C modes is bigger slightly. Therefore, it may be presumed that the action force between the terminal oxygen and atoms around is not evidently alteration with side-uprightness, obverse-uprightness and obverse-face modes, except terminal oxygen in the system with side-face-combination-B mode.

The average value of gross population of bridge oxygen in the system with obverse-face-combination-D mode is the lowest. Totally, the change trend of the average values is side-uprightness-combination-A > side-face-combination-B > obverse-uprightness-combination-C > obverse-face-combination-D. It may be presumed that the activity of bridge oxygen in the system with obverse-face-combination-D mode is

larger than those of the other three combination modes.

It can be seen from Fig.4 that, the change trend of the atomic gross population of the studied systems is coincidence on the whole.

At the same time, the total energy of the obverse-face-combination-D mode is relatively lower, and from the point of view of energy, this combination mode is probably more possible than the other combination modes (Table 1). Whereas from the point of view of the change trend of the same kind of atomic gross population, the effect on atomic gross population of the side-face combination mode is the most distinct, so that it should be preliminarily presumed from Fig.3 and Fig.4 that the interatomic bond force of the system with side-face-combination-B mode may be weaker to a certain extent.

From the point of view of statistics, the systems will come up to mechanical equilibrium in the process of the unit combination. Thereby it may be supposed that the microscopic character may be what is called fluctuation.

3.2 Atomic charge

The average values of atomic charge of atoms in the systems of four typical combination modes and single unit were calculated at RB3LYP/6-31G and RHF/6-31G levels. According to the calculation results, the average values of total atomic charge of aluminum, terminal oxygen and bridge oxygen in the four typical combination modes and single unit were calculated. Figs.5 and 6 show the results calculated at RB3LYP/6-31G and RHF/6-31G levels respectively.

It can be seen from Figs.5 and 6 that, the average values of the four typical combination modes and the single unit are some shade different after unit combination.

The difference in average values of atomic charge of aluminum, terminal oxygen and bridge oxygen is not apparent between those atoms in obverse-uprightness-combination-C mode and those in single unit. That is to say, the obverse-uprightness combination does not lead to the apparent alteration of interatomic bond force.

The difference in average values of atomic charge of terminal oxygen and bridge oxygen is also not apparent between those atoms in side-uprightness-combination-A modes and in single unit, but the

average values of atomic charge of aluminum are lessened to some extent and it can be thought that the bond force between aluminum and the other atoms around is possibly lessened.

The average values of atomic charge of terminal oxygen and bridge oxygen in the system with side-face-combination-B mode are apparently larger than those in single unit, that is to say, the negative charge is decreased and the ability to gain electron is decreased. It might be thought theoretically that the bond force between terminal oxygen and bridge oxygen and the other atoms around is lessened.

The average values of atomic charge of aluminum in the system with obverse-face-combination-D mode are apparently larger than those in single unit, but the average values of atomic charge of terminal oxygen and bridge oxygen are lessened to a great extent, that is to say, the net charge of aluminum is more positive and the net charges of terminal oxygen and bridge oxygen are more negative, and therefore the activity of the interatomic electron transformation is lessened. It may be of the opinion that from the point of view of the net charge, when the combination mode is obverse-face-combination-D,

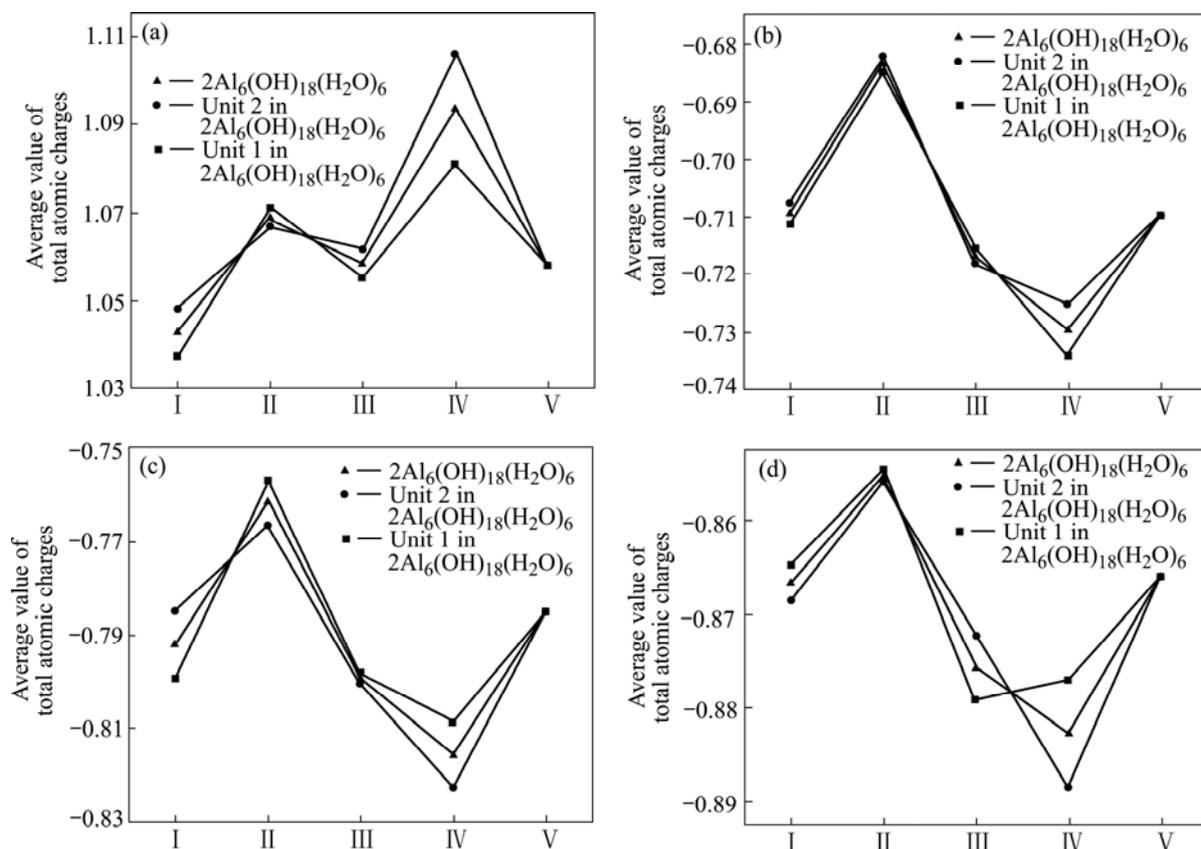


Fig.5 Average values of total atomic charges on Al(a), terminal oxygen in Al-H₂O (b), terminal oxygen in Al-OH (c) and bridge oxygen(d) of systems calculated at RB3LYP/6-31G level(I represents combination-A; II represents combination-B; III represents combination-C; IV represents combination-D; V represents single growth unit)

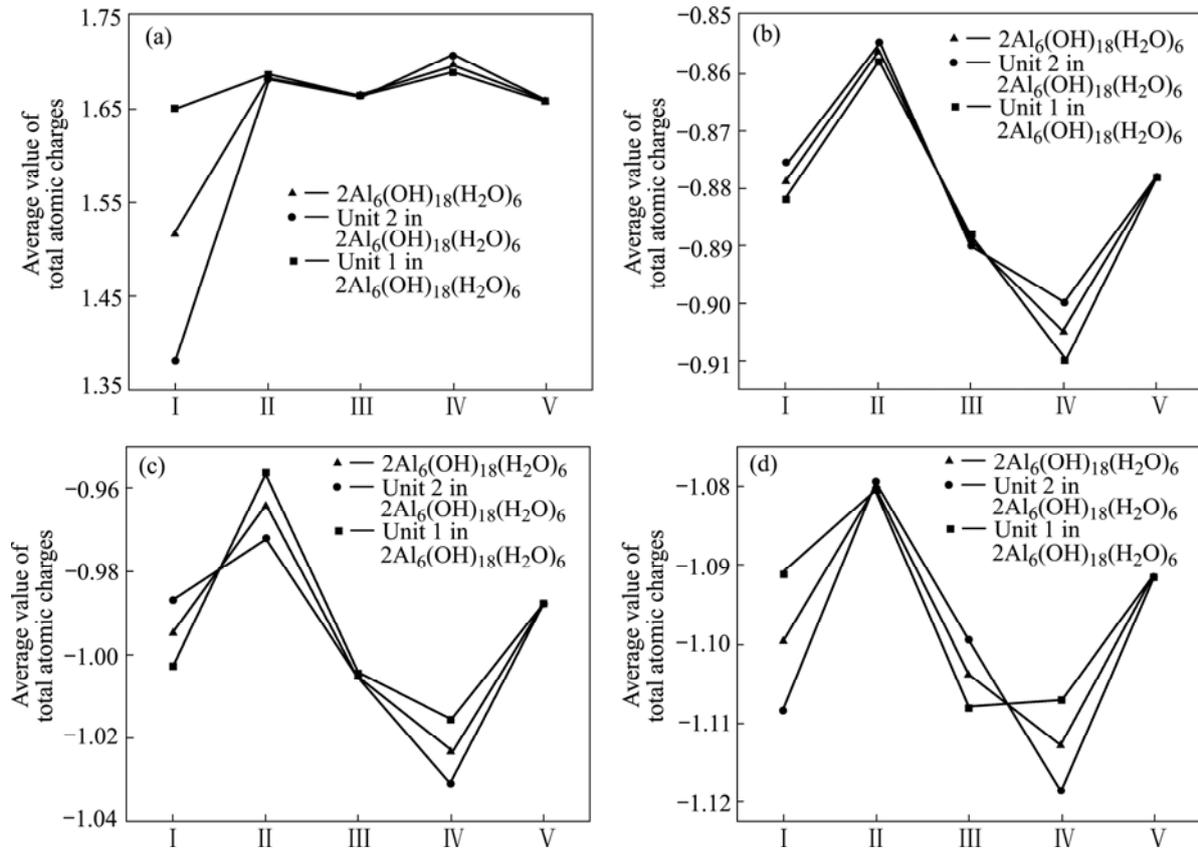


Fig.6 Average values of total atomic charges on Al(a), terminal oxygen in Al-H₂O (b), terminal oxygen in Al-H₂O (c) and bridge oxygen(d) of systems calculated at RHF/6-31G level (I represents combination-A; II represents combination-B; III represents combination-C; IV represents combination-D; V represents single growth unit)

the interatomic bond force will be enhanced.

4 Conclusions

1) The combination mode of the crystal growth unit of Al(OH)₃ makes a difference in the relative intensity of chemical bond and transforming connection of interatomic electron.

2) The quantum chemistry calculations were performed at RB3LYP/6-31G and RHF/6-31G levels respectively. From the point of view of bond population, it is preliminarily presumed that the interatomic bond force of the system with side-face-combination-B mode is weaker to a certain extent. From the point of view of the net charge, when the combination mode is obverse-face-combination-D, the interatomic bond force will be enhanced.

References

- [1] STAHLIN W. Alumina morphology and particle strength[J]. *Light Metals*, 1985: 423–432.
- [2] PONS M.N. Particle morphology: from visualization to measurement[J]. *Powder Technology*, 1999, 103(1): 44–57.
- [3] SANG J.V. Factors affecting the attrition strength of alumina products[J]. *Light Metals*, 1987: 121–127.
- [4] FRANCES C. Particle morphology of ground gibbsite in different grinding environments[J]. *Mineral Processing*, 2001, 6(1): 41–56.
- [5] BELAROU K. Morphological characterization of gibbsite and alumina[J]. *Powder Technology*, 2002, 127(3): 246–256.
- [6] STEPHANE. Attrition of hydrargillite: mechanism and quantification of particle fragility by a new attrition index[J]. *Powder Technology*, 1993, 75(3): 49–57.
- [7] BARONI T.C. Correlation between charge contrast imaging and the distribution of some trace level impurities in gibbsite[J]. *Microscopy and Microanalysis*, 2000, 6(2): 49–58.
- [8] ROBERTS K.J. Predicting particle morphology on the basis of the root molecular and crystal structure[J]. *Solid State and Materials Science*, 1996, 1: 506–513.
- [9] SWEEGERS C. Morphology, evolution and other characteristics of gibbsite crystals grown from pure and impure aqueous sodium aluminate solutions[J]. *Journal of Crystal Growth*, 2001, 233(4): 567–582.
- [10] LI Jie. Study on the Structure Characteristics and Decomposition Mechanism of Supersaturated Sodium Aluminate Solution[D]. Changsha: Central South University, 2001. (in Chinese)
- [11] LI Jie, CHEN Qi-yuan. Investigation on the mode of the growth unit for alumina trihydrate crystals precipitation from supersaturated sodium aluminate solution[A]. *Hydrometallurgy, ICHM'98[C]*. China: Kunming, 1998. 240–244.
- [12] LI Jie, CHEN Qi-yuan, YIN Zhou-lan. Studies on the kinetics of unseeded nucleation of aluminum trihydroxide from supersaturated sodium aluminate solutions[J]. *Chemical Journal of Chinese University*, 2003, 24(9): 1652–1656. (in Chinese)
- [13] LI Jie, CHEN Qi-yuan, YIN Zhou-lan, ZHANG Ping-min.

- Development and prospect in the fundamental research on the decomposition of supersaturated sodium aluminate solution[J]. *Progress in Chemistry*, 2003, 15(3): 170—177. (in Chinese)
- [14] CHEN Qi-yuan, LI Jie, YIN Zhou-lan, ZHANG Ping-min. Decomposition of supersaturated sodium aluminate solution[J]. *Trans Nonferrous Metals Soc China*, 2003,13(3): 649—654.
- [15] CHEN Qi-yuan, ZHOU Jun, LI Jie, YIN Zhou-lan. Transformation of monomer aluminate ions from tetranedron to octaheron[J]. *Trans Nonferrous Metals Soc China*, 2003,13(4): 972—976.
- [16] CHEN Qi-yuan, LI Jie, YIN Zhou-lan, ZHANG Ping-min. Study on the kinetics and mechanism of the homogeneous nucleation of $\text{Al}(\text{OH})_3$ crystal from supersaturated aluminate solution[J]. *Metallurgical and Materials Transaction B*, 2005, 38(3): 249—252.
- [17] LI Jie, CHEN Qi-yuan, YI Zhou-lan. Influence of supersaturation on structure of sodium aluminate solutions with mediate concentration: a solution X-ray diffraction study[J]. *Trans Nonferrous Met Soc China*, 2002, 12(5): 992—996.
- [18] WU Zheng-ping, CHEN Qi-yuan, YIN Zhou-lan, LI Jie. Ab initio and DFT studies on the structure and bonding orientation of the favorable growth unit $\text{Al}_6(\text{OH})_{18}(\text{H}_2\text{O})_6$ of $\text{Al}(\text{OH})_3$ crystals precipitating I[J]. *Journal of the Chinese Rare Earth Society*, 2004, 22(Special Issue): 283—288. (in Chinese)
- [19] WU Zheng-ping, CHEN Qi-yuan, YIN Zhou-lan, LI Jie. Ab initio and DFT studies on the structure and bonding orientation of the favorable growth unit $\text{Al}_6(\text{OH})_{18}(\text{H}_2\text{O})_6$ of $\text{Al}(\text{OH})_3$ crystals precipitating II[J]. *Journal of the Chinese Rare Earth Society*, 2004, 22(Special Issue): 289—293. (in Chinese)
- [20] WU Zheng-ping, CHEN Qi-yuan, YIN Zhou-lan, LI Jie. Studies on the structure and bonding orientation of the favorable growth unit $\text{Al}_6(\text{OH})_{18}(\text{H}_2\text{O})_6$ of gibbsite[J]. *Trans Nonferrous Met Soc China*, 2005, 15(3): 671—679.
- [21] WU Zheng-ping, CHEN Qi-yuan, YIN Zhou-lan, LI Jie. Effects of the combination modes of the favorable growth unit of $\text{Al}(\text{OH})_3$ crystals precipitating on Van der Waals and chemical bond force[J]. *Trans Nonferrous Met Soc China*, 2005, 15(4): 913—921.

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