MODELLING OF THE BRUCITE SHEET IN LIZARDITE

EVA SCHOLTZOVÁ, DANIEL TUNEGA, LADISLAV TURI NAGY

*Institute of Inorganic Chemistry, Slovak Academy of Sciences,
Dúbravská cesta 9, 842 36 Bratislava, Slovak Republic*

The effect of different terminations of cluster models was shown on the quantum-chemically calculated atomic charges, bonding population analysis and harmonic vibrational frequency of the inner OH group. As the basic model was proposed 32 atomic cluster of the brucite sheet in lizardite layer. The calculations were performed using Hartree-Fock method and 3-21G atomic basis set (HF/3-21G).

INTRODUCTION

The layer silicates similarly as zeolites attract great attention due to their important role as selective catalysts, adsorbents, and ion exchangers. An increasing use of layer silicates for industrial purposes stimulates both, experimental and theoretical studies aiming to understand the structure and properties of such systems. It is necessary to emphasize that many experiments are temporally and financially pretentious and suitably performed calculations can provide valuable information at considerable saving of the time and money.

Two important factors mainly affect the quality and the reliability of calculated properties. The first one is the choice of some appropriate quantum-chemical method together with adequate basis set. The second one is a proposal of some suitable model sufficiently representing the real structure. In a treatment of solids like phyllosilicates are, the problem is in their infinity. There are two basic approaches in solving this situation. The first approach is based on using of the translational symmetry of solids in calculation procedure [1-4]. However, the periodical models of layer silicates can contain many atoms in the computational cell and this is the reason why the computational demands can be extremely high, especially when larger atomic basis sets are used. This approach was used in the study of the electron structures of lizardite [5] and brucite [6, 7]. The effect of the basis set on the atomic charges and the electron density in the simple tetrahedral sheet $^\infty[Si_2O_5]^{2-}$ was also studied by this method in [8]. The second approach - cluster modelling - is based on using of some atomic cluster of finite size. Such cluster is treated then as a molecule. Cluster models would be proposed to reflect characteristic features of original structures. The problem of the infinity of the system modeled can be solved by the use of suitable termination of dangling bonds of the model cluster and/or including the effect of the "missing" rest of the solid into the computational procedure, respectively. Various methods of cluster termination and also various techniques of embedding of

the cluster in the rest of the solid have been proposed. These methods and techniques vary according the chemical character of the system modeled. The cluster-model approach is used very intensively in the alumino-silicate field. The outcome of this is a lot of published works. We can mention here above all the main review papers of Sauer [9, 10], Lasaga [11], Gibbs [12] and Tossell [13]. These works summarized methods and approaches used above all in the study of the zeolites. Surprisingly, only a few theoretical works deal with quantum-chemical calculations on cluster models of layer silicates. One of the first works, which was directly oriented on layer silicate structures, was the cluster model study of the geometrical deformations in the layers of gibbsite, brucite and serpentine using CNDO/2 method [14]. In the work [15] the authors studied the isomorphic substitution of the octahedral central cations in the dioctahedral smectites. The adsorption of the water molecule on the surface of the montmorillonite layer was studied by MINDO/3 [16, 17]. Several cluster models were used in the theoretical study in [18, 19].

The simple cluster approach without using of sophisticated embedding scheme meets the problem of the cluster termination. The dangling bonds arising on the frontier of the cluster would be saturated in some way. Some suitable atoms can be used for this purpose. These atoms have to be chosen in such way that the chemical quality of the original system is conserved in a maximum possible extent. Simultaneously, the size of the model cluster could be such, that the frontier of the cluster will only minimally affect the studied characteristics. Brand and Chamot have discussed this problem [20, 21] in the systematic study of the dependence of the OH stretching frequency in ZSM-5 zeolite on the size of the cluster models. They have found the optimized structure of the central Si-OH-Al bridge appeared to converge with the addition of the third coordination shell of atoms around the central bridge. Another problem arises with the occurrence of possible charge of the cluster. The non-stoichiometry of the cluster or the non-stoichiometry caused by the actually used method of saturation of the

dangling bonds can lead to highly charged clusters. This charge is necessary to compensate, otherwise the electron properties of the model will be strongly influenced by the artificially involved charge, especially, an electron instability can arise in negatively charged model.

In the present paper the cluster approach is used for modelling of the brucite sheet in layer silicates. Several possible terminations of the basic cluster are examined. The effect of the various terminations of the cluster and various compensations of the cluster charge on the electron structure and valence vibration frequency of the inner hydroxyl group is shown. The selection of the most appropriate cluster termination of the brucite sheet in lizardite is based on the evaluation of the changes in the distribution of the charges on the inner atoms of the cluster, the calculated harmonical frequency of the stretching vibration of the inner OH group and the bonding population analysis. This selected model will be used in the forthcomming work concerning the effect of the substitutions in the octahedral sheet of the layer silicates on their electron structure and OH vibrational frequency.

METHOD

Quantum-chemical procedure and basis set

The quantum-chemical calculations were performed using GAUSSIAN94 program [22]. With respect to the size of the cluster models and the studied properties (the atomic charges, the bonding population analysis and the harmonic frequency of the stretching vibration of the inner OH group) the Hartree-Fock method and 3-21G atomic basis set were chosen. The size of the model systems (our biggest model consists of 32 atoms and 221 basis functions) together with limited computational capabilities leads to compromise between the size of the model and the size of the basis set. The 3-21G basis set is sufficient for reaching the goals of present work described above (our aim is not to observe the influence of the size of the basis set on the calculated properties). The force constant of the harmonic frequency of the stretching vibration of the inner OH group was obtained using step by step optimization of the inner OH bond distance (by step 0.005 Å) and by subsequent curve fitting through the calculated points. The atomic charges and bonds were obtained from Mulliken population analysis.

MODELS

Atomic coordinates of the cluster model were derived from the experimentally determined structural parameters of 1:1 trioctahedral mineral lizardite [23] (figure 1). The basic model (figures 2, 3) was constructed as follows: The representative part of the structure from the brucite sheet of the lizardite was cut. The inner OH group was positioned into the centre of the cluster. Our

system is system with localised electron structure and ionic (Mg-O) and polar covalent (Si-O, O-H) bonds, so the cluster approach is fully justified. The experimental structure is characterized by mutually connected tetrahedral and octahedral (brucite-like) sheets. The octahedral sheet is connected with tetrahedral sheet through apical oxygen atoms from one side and terminated by outer OH groups from another one. The positions of the hydrogen atoms from outer OH groups were determined by OH bond distance 0.95 Å vertical towards outer oxygen plane, because it is very difficult to determine the exact positions of hydrogen atoms from the diffraction data. The broken bonds of the apical oxygen atoms were saturated by adding the hydrogen atoms using the OH bond distance 0.95 Å.
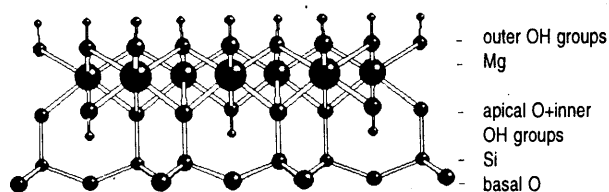

- outer OH groups
- Mg
- apical O+inner OH groups
- Si
- basal O

Figure 1. [010] view of structure of lizardite.

inner atoms of the cluster

Figure 2. Basic cluster model.

- outer OH groups
- Mg
- apical O
- terminal H

Inner OH group
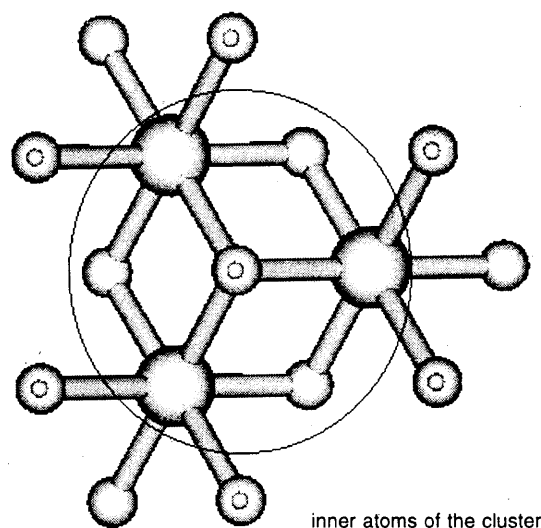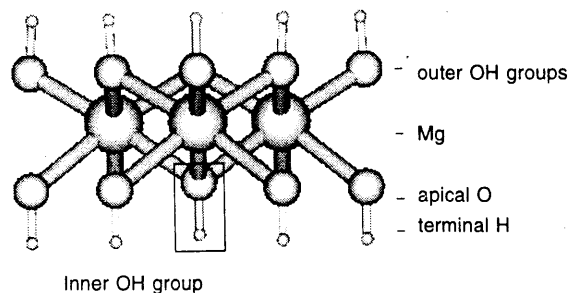
Figure 3. Basic cluster model - 90° rotated.

The basic cluster constructed using the above procedure has summary formula $\{Mg_3O_{13}H_{13}\}^{-7}$. This cluster possesses high negative charge (-7). This charge was compensated using various terminations of the cluster. The nonphysically high charge is compensated by convenient combination of the positive or negative charges in the positions of the atoms of the missing structure. However, one has to keep in mind that such termination could result in high polarisation of the model, mainly on the boundary of the cluster. The termination of the cluster by hydrogen atoms or another atoms is most suitable, if possible. Six models of the brucite sheet of the lizardite were proposed: the basic cluster without termination of dangling bonds (MG) and without compensation of the charge -7; two models terminated by nine equal point charges positioned in the positions of the missing atoms. The magnitude of these point charges was chosen to obtain the summary charge of the cluster -1 (Q1) and 0 (Q0), respectively; one model terminated by six hydrogen atoms (HH) in the O-H distance 0.95 Å with summary charge -1; one model terminated by three magnesium atoms in the positions of the missing atoms (MGMG) with summary charge -1 and finally one model terminated by three magnesium atoms and six point charges in the position of the missing atoms (MGQ) with summary charge 0. Table 1 summarizes all proposed models.

Table 1. The designation of the cluster models.

Symbol	Description
MG	$\{Mg_3O_{13}H_{13}\}^{-7}$, summary charge $\{-7\}$
Q1	$\{Mg_3O_{13}H_{13}\}^{-7}$ + 9 point charges (0.6667), positioned in the position of the missing atoms, summary charge $\{-1\}$
Q0	$\{Mg_3O_{13}H_{13}\}^{-7}$ + 9 point charges (0.7778) positioned in the position of the missing atoms, summary charge $\{0\}$
MGMG	$\{Mg_3O_{13}H_{13}\}^{-7}$ + 3Mg , summary charge $\{-1\}$, Mg atoms positioned in the position of the missing atoms
MGQ	$\{Mg_3O_{13}H_{13}\}^{-7}$ + 3Mg + 6 point charges, summary charge $\{0\}$, atoms and point charges positioned in the position of the missing atoms
HH	$\{Mg_3O_{13}H_{13}\}^{-7}$ + 6H , summary charge $\{-1\}$, H atoms positioned on the distance O-H = 0.95 Å

RESULTS AND DISCUSION

The choice of models, in which the artificial effects on calculated properties are minimal, was done according following criteria: a) evaluation of the changes in the distribution of the charges on the inner atoms of the

clusters (the atoms of the inner OH group, the central atoms in the octahedrons - three magnesium atoms, and three oxygen atoms from the outer OH groups. All these atoms are referenced as "inner" atoms (figure 2); b) the bonding population analysis of the bonds O_a-H and Mg-O_i (where $i = a, b$; O_a is atom from the inner OH group, O_b atoms are from the outer OH groups, which are the nearest to the inner OH group; c) the harmonic frequency of the stretching vibration of the inner OH group.

Distribution of the charges on the inner atoms of the models

Table 2 shows the average value of the charges for all magnesium atoms and oxygen atoms of the outer OH groups because their mutual positions are symmetrical. Type of termination of the clusters does not influence expressively the distribution of the charges on the atoms of the inner OH group. One can see, that difference between the lowest and highest value of the charge on O_a atom is only 0.04 |e| (in the units of the electron charge). The reason is, that atoms of the inner OH group are relatively far from the cluster border (over two interatomic bonds). Different situation is in the case of Mg and O_b atoms. Mainly the charges on Mg atoms differ considerably (0.4 |e|). This is caused by the positions of the Mg and O_b atoms, which lie nearly the frontier of the cluster and so the electron structure around these atoms is significantly affected by the cluster termination. On the base of the results in the table 2 the models can be separated on three groups according to the values of the charges on the Mg and O_b atoms. The first group is represented by MG model (basic model). Models terminated with point charges (Q0 and Q1) are in the second group and models terminated with atoms (MGMG, HH) or combination of atoms and point charges (MGQ) are in the third group. Surprisingly, very low values of the charges on Mg atoms are in the models Q1 and Q0. All three models from the third group are acceptable from point of view of ionic character of the Mg-O bond.

Table 2. The distribution of the Mulliken charges on the inner atoms.

	Mg	O_b	O_a	H_a
MG	0.46	-0.79	-0.84	0.31
Q1	0.30	-0.89	-0.87	0.36
Q0	0.26	-0.88	-0.87	0.37
HH	0.64	-0.92	-0.86	0.36
MGMG	0.66	-0.90	-0.88	0.41
MGQ	0.62	-0.90	-0.88	0.41

Bonding Mulliken population analysis (table 3)

Bonding population analysis of the bonds Mg-O$_a$ (bond length 2.082 Å), Mg-O$_b$ (bond length 2.008 Å) and O$_a$-H (optimized bond length 0.96 Å) is next criterion in the evaluation of the models. Likewise as in the case of the distribution of the charges on the atoms, the results from this analysis show the same trend of the influence of the cluster termination. The values of the Mg-O$_b$ bond populations are more sensitive to the type of the cluster model termination. The models can be separated on the two groups according to obtained values of Mg-O$_b$ bond populations. The first group contains MG, Q1 and Q0 models and the second one contains the rest three models. Only minimal changes are observed in O$_a$-H bond population and no changes are observed in the population of Mg-O$_a$ bonds.

Table 3. The bonding Mulliken population analysis on the bonds Mg-O$_a$=2.082 Å , Mg-O$_b$=2.008 Å , O$_a$-H= 0.96 Å.

	Mg-O$_a$	Mg-O$_b$	O$_a$-H
MG	0.10	0.11	0.24
Q1	0.10	0.12	0.25
Q0	0.10	0.12	0.25
HH	0.10	0.05	0.23
MGMG	0.10	0.06	0.25
MGQ	0.10	0.06	0.25

Harmonic frequency of the stretching vibration of the inner OH group (table 4)

The calculated harmonic frequencies of the stretching vibration of the inner OH group vary within the range of 130 cm^{-1} depending on the type of the cluster. It is generally known that the HF method gives too high values of calculated vibrational frequencies in comparison with experimental data. Calculated values are often scaled for the purpose of the comparison with experimental results. The value of the scaling factor depends on the used method, atomic basis set and the type of the vibration. In our work the scaling factor of the value 0.9085 was taken from the literature [24]. This value was obtained on the set of the 22 different molecules and set of 1066 frequencies at HF/3-21G level of theory. The results in the table 4 shows, that the models can be separated again on the three groups, but slightly different from the first case. The vibrational frequency of the inner OH group from the MG model is in the first group, the frequencies of the Q1, Q0, HH and MGMG model are in the second one, and the frequency of MGQ model is in the last one. The scaled frequency

of the MGQ model (3684 cm^{-1}) is the nearest to the experimental value of the stretching vibration of the inner OH group in the lizardite (3660 cm^{-1}) [25].

All examined properties show that models MGMG, MGQ and HH give mutually similar results, nevertheless sufficiently different from the results of the rest models. The argument for the benefit of the models MGMG, MGQ, and HH is the fact, that these models provide both, good agreement of the vibration frequency with experiment and the relatively high absolute values of charges on the Mg atoms. This result is in accordance with generally accepted idea of ionic character of the brucite sheet [7]. It must be note, that calculated charges depend on used basis set, and e.g. including polarisation functions into the basis set of Mg atom shifts its charge to higher value, what else ephasizes the ionic character of the Mg-O bond.

Table 4. Force constants f and stretching frequencies of inner OH group $\bar{v}$, $\bar{v}_s$ - scaled, for the individual clusters.

	f (J m^{-2})	$\bar{v}$ (cm^{-1})	$\bar{v}_s$(cm^{-1})*
MG	31.23	3912	3554
Q1	32.03	3962	3600
Q0	32.14	3969	3606
HH	32.28	3978	3614
MGMG	32.38	3983	3619
MGQ	33.54	4055	3684

* scaled frequency: scaling factor = 0.9085 [24] Experimentally obtained frequency: 3660 cm^{-1} [25]

CONCLUSION

It was shown, that models MGQ, MGMG and HH provide acceptable results for the studied system. The effect of the cluster termination on calculated properties and on the electron structure in the central part of the cluster is the least for these models. They are suitable for the use in the next study of the changes in the electron structure of the layer silicates at isomorphic substitutions of the central atoms in octahedral sheet of layer silicates.

Acknowledgement

References

1. Bleam W.F., Hoffmann R.: Phys. Chem. Minerals *15*, 398 (1982).
2. Pisani C., Dovesi R., Roetti C.: *Hartree-Fock ab initio Treatment of Crystalline Systems.* Lecture Notes in Chemistry 48, Springer-Verlag, Berlin 1988.

3. D` Arco Ph., Sandrone G., Dovesi R., Orlando R., Saunders V.R.: Phys. Chem. Minerals *20*, 407 (1993).
4. Valerio G., Catti M., Dovesi R., Orlando R.: Phys Rev B *52*, 2422 (1995).
5. Smrčok Ľ., Benco Ľ.: Am. Mineral. *81*, 1405 (1996).
6. Sherman, D. M.: Am. Mineral. *76*, 1769 (1991).
7. D` Arco P., Causa M., Roetti C., Silvi B.: Phys Rev B *47*, 3522 (1993).
8. Benco Ľ., Smrčok Ľ.: Phys. Chem. Minerals *21*, 101 (1994).
9. Sauer J., Ugliengo P., Garrone E., Saunders V.R.: Chem. Rev. *94*, 2095 (1994).
10. Sauer J.: Chem. Rev. *89*, 199 (1989).
11. Lasaga A.C.: Reviews of Geophysics *30*, 269 (1992).
12. Gibbs G.V.: American Mineralogist *67*, 421 (1982).
13. Tossell J.A.: Phys. Chem. Minerals *59*, 319 (1987).
14. Peterson R.C., Hill R. J. Gibbs G. V.: Canadian Mineralogist *17*, 703 (1979).
15. Aronowitz S., Coyne L., Lawless J., Rishpon J.: Inorg. Chem. *21*, 3589 (1982).
16. Delville A.: Langmuir *7*, 547 (1992).
17. Delville A.: Langmuir *8*, 1796 (1992).
18. Tunega D., Turi Nagy L.: Ceramics-Silikáty *37*, 145 (1993).
19. Tunega, D., Turi Nagy, L., Varga, Š.: Chem. Papers *47*, 273 (1993).
20. Brand H., Curtiss L. A.: J. Phys. Chem. *96*, 7725 (1992).
21. Chamot E.: in *Molecular Modeling of Petroleum Processes and Catalysis*; Division of Petroleum Chemistry, Inc., American Chemical Society: San Francisco 1992.
22. Frisch M.J., Trucks G.W., Schlegel H.B. et al.: Gaussian 94, Revision D.3 Gaussian, Inc., Pittsburgh PA, 1995.
23. Mellini M.: Am. Mineral. *67*, 587 (1982).
24. Scott A.P., Radom L.: J. Phys. Chem. *100*, 16502 (1996).
25. *Atlas of Infrared Spectroscopy of Clay Minerals&their Admixtures*, Ed. van der Marel H. W., Beutelspacher, Elsevier, 1976.

Submitted in English by the authors.

MODELOVANIE BRUCITOVEJ VRSTVY V LIZARDITE

EVA SCHOLTZOVÁ, DANIEL TUNEGA, LADISLAV TURI NAGY

Ústav anorganickej chémie SAV,
Dúbravská cesta 9, 842 36 Bratislava, Slovenská republika

Pri výpočte elektrónovej štruktúry brucitovej vrstvy v lizardite sa použil klastrový prístup. Šesť spôsobov ukončenia klastra sa vyhodnotilo na základe kvantovo-chemicky počítaných atómových nábojov, väzbovej populačnej analýzy a harmonickej vibračnej frekvencie vnútornej OH skupiny. Výpočty sa uskutočnili na *ab initio* úrovni metódou Hartreeho-Focka s 3-21G bázou (HF/3-21G). Ako najvhodnejšie sa ukázali modely s ukončením klastra vo forme atómov a minimálnym (MGMG, HH) resp. nulovým (MGQ) celkovým nábojom. Tieto tri modely sú vhodné pre ďalšie sledovanie vplyvu substitúcií oktaédrických katiónov na zmenu harmonickej frekvencie valenčnej vibrácie vnútornej OH skupiny v tri- a dioktaédrických vrstevnatých silikátoch.