Semiempirical Quantum-Chemical Calculation of Electrostatic Potential Generated by Idealized Layer of Talc

[a]D. TUNEGA, [b]L. TURI NAGY, and [b]Š. VARGA

[a]*Department of Physical Chemistry, Faculty of Chemical Technology, Slovak Technical University, SK-812 37 Bratislava*

[b]*Institute of Inorganic Chemistry, Slovak Academy of Sciences, SK-842 36 Bratislava*

Received 20 November 1992

The electrostatic potential of an isolated layer of talc $Mg_3Si_4O_{10}(OH)_2$ in idealized structure (layer group symmetry *p6mm*) was computed using the electron distribution obtained from semiempirical INDO/2 calculation. Cluster of 9348 atoms generated by translational multiplication of identical replicas of a basic motive was used as a model of the two-dimensional infinite layer. The basic motive was selected from the innermost part of the 298 atom layer on which the electronic structure calculations were performed. The model cluster was chosen so as to preserve the symmetry of the whole system, and to include all the non-negligible contributions of the entire layer to the electrostatic potential in the chosen region, with a sufficient accuracy. The knowledge of the electrostatic potential enables to obtain harmonic frequencies of vibration of a proton hypothetically adsorbed *in vacuo* on the surface of the ideal layer of talc.

The main goal of this paper is to map the electrostatic potential in the vicinity of a single idealized layer of talc. The layer silicate — talc ($Mg_3Si_4O_{10}(OH)_2$) was chosen as a model representing the very important group of 2 : 1 trioctahedral layer silicates. The single layer in these minerals consists of one octahedral sheet placed between two tetrahedral sheets (Fig. 1).

The dominant component of the interaction potential of a nonbonding interaction is its electrostatic part. The electrostatic potential, being a component of the interaction with the longest range, has the decisive role in the process of orientation of an adsorbate when approaching the surface.

Therefore, the aim of many calculations concerning the silicate chemistry is to obtain sufficiently good description of the behaviour of the interaction potential of investigated silicate systems. For example, papers [1—3] are devoted in particular to description of the interactions of molecules and ions in zeolitic pores. Papers [4, 5] deal with the electrostatic potential generated by the surface of model layered silicates. There are studied both idealized layers and various deformed and isomorphically substituted structures as well in these papers. The electrostatic potentials obtained in these works were calculated in the approximation of atomic point charges taken from quantum-chemical computations using the Extended Hückel Theory (EHT) method [6].

It is a well-known fact that the EHT method overestimates the magnitudes of atomic charges and leads to inadequately polar bonds. Moreover, the electrostatic potential computed from the atomic point charges obtained by the molecular orbital pro-

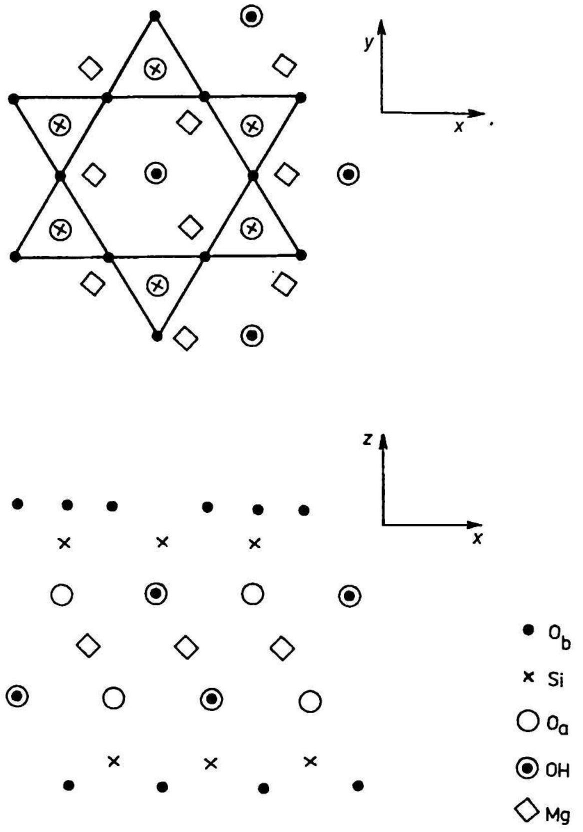

Fig. 1. The structure of an idealized talc layer. For the *x*—*y* projection only the upper tetrahedral sheet is depicted.

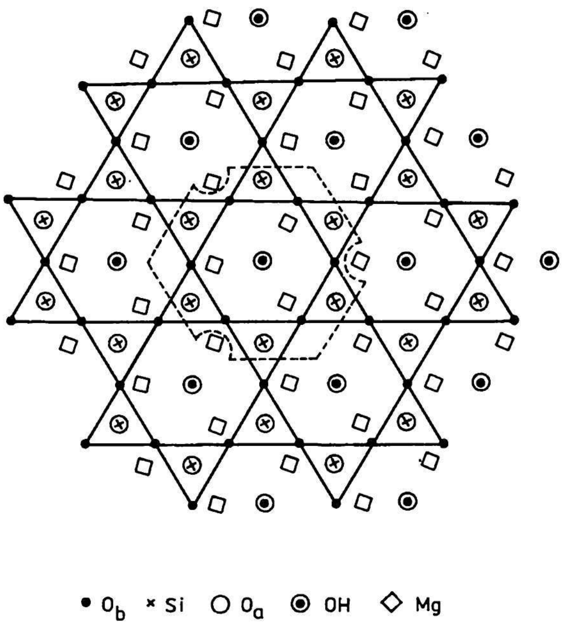

Fig. 2. The 298-atom cluster of a single talc layer. The central part of it is drawn (- - - -). For clarity only the upper tetrahedral sheet is depicted.

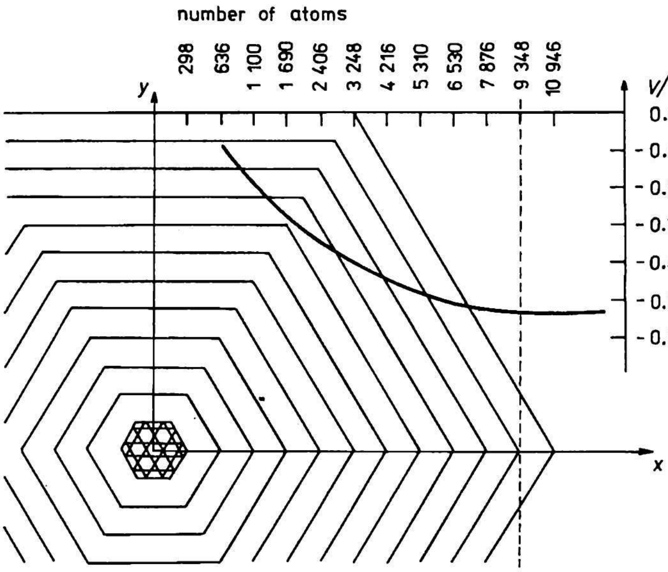

Fig. 3. The dependence of the electrostatic potential on the cluster size in the chosen point (see the text). The 298-atom cluster used for the semiempirical calculation is also depicted.

cedure is far from being a reasonable approximation of the electric field generated by the system [7]. The proper description of the electric field in the vicinity of a molecule can be obtained either using the multipole expansion [7] or by direct computation using the exact definition [8]

$$V(\boldsymbol{r}) = \sum_{A} \frac{Z_A}{|\boldsymbol{r} - \boldsymbol{R}_A|} - \int_{V_1} \frac{\rho(\boldsymbol{r})}{|\boldsymbol{r} - \boldsymbol{r}_1|} \mathrm{d}V_1 \qquad (1)$$

where the summation runs over all atoms of the studied system, Z_A is the core charge, $\boldsymbol{R}_A$ is the positional vector of the A-th atom, ρ is the electron density, and the integration over the infinite volume is understood. The expression (*1*) can be modified in accordance with approximations used in computation of the electron density, and according to the required accuracy of the computation of the electrostatic potential [8]. Such modifications are expected to provide more realistic description of the electrostatic potential generated by the layer of a phyllosilicate.

METHOD

The relation (*1*) modified according to the Giessner-Prettre-2 (GP2) approximation [8] into the form

$$V(\boldsymbol{r}) = \sum_{A} \frac{Z_A}{|\boldsymbol{R}_A - \boldsymbol{r}|} - \sum_{\mu} P_{\mu\mu} V_{\mu\mu}(\boldsymbol{r}) \qquad (2)$$

was used for the calculation of the electrostatic potential. The indices A and μ run over all the atoms and all atomic orbitals of the system, respectively. $P_{\mu\mu}$ are diagonal elements of the electron density matrix and integrals $V_{\mu\mu}(\boldsymbol{r})$ are defined by

$$V_{\mu\mu}(\boldsymbol{r}) = \int_{V_1} \chi_{\mu}^{*}(\boldsymbol{r}_1) \frac{1}{|\boldsymbol{r} - \boldsymbol{r}_1|} \chi_{\mu}(\boldsymbol{r}_1) \mathrm{d}V_1 \qquad (3)$$

where χ_μ are atomic orbitals. The approximation (*2*) is compatible with the use of semiempirical Zero-Differential-Overlap (ZDO) type quantum-chemical methods for computation of the electron structure.

The values $P_{\mu\mu}$ were obtained by quantum-chemical computations [9] using the semiempirical Intermediate Neglecting of Differential Overlap (INDO/2) method for the cluster of 298 atoms. The details of this calculation are described elsewhere [10].

The central part of this cluster (Fig. 2) was selected as the base for the further calculations. This innermost part of the cluster can be considered to give a reasonable picture of the electron structure of the interior of two-dimensional infinite talc layer [10]. Consequently, the electron densities, obtained for these atoms from the centre of the cluster were used for all the symmetry equivalent atoms of the 9348-atom layer model, when computing the contributions to the electrostatic potential.

The expression (*2*) contains the summation of slowly converging Coulombic terms. This is why such a large cluster was used as a model of the idealized layer of talc for the calculation of the electrostatic potential. The choice of the cluster size was determined by testing the dependence of the electrostatic potential in the considered volume on the

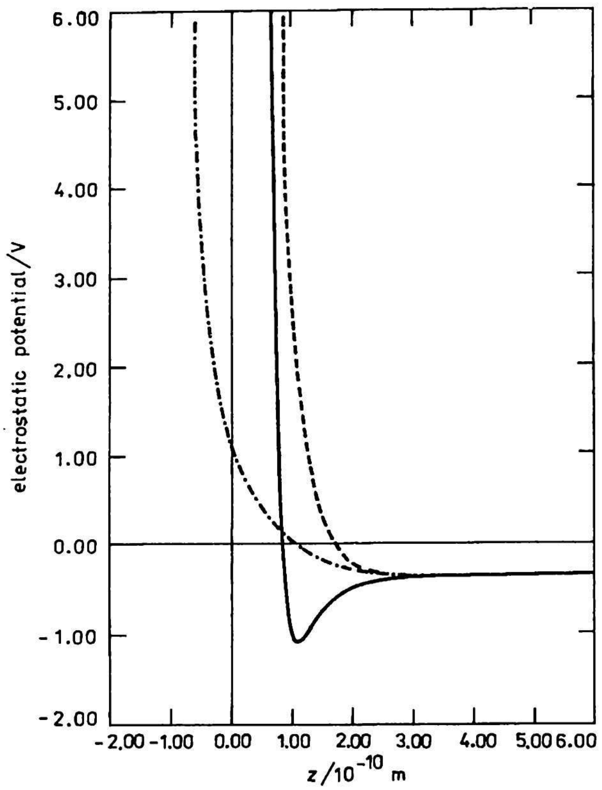

Fig. 4. The dependence of the electrostatic potential on the distance from the layer for the three special verticals to the layer (on the top basal oxygen atom, silicon atom, and OH group). ——— O_b, - - - - Si, —·—·— OH.

cluster size. Fig. 3 shows this dependence for the point in the bottom corner of the tabulation grid (see text below). From all the points of the studied volume this point is assumed to be the position with the highest sensitivity of the potential to the change of the cluster size. As can be seen from Fig. 3, the dependence is already saturated for the 9348-atom cluster. The difference between potentials of 9348- and 10946-atom clusters is less than 10^{-3} V. All the examined clusters were generated so as to preserve the electroneutrality and the symmetry of the complete layer.

The electrostatic potential behaviour was studied in a region of space above the layer, which was chosen to have the form of a rectangular parallelepiped; its ground plane covering one complete period of identity of the layer plus a small necessary surrounding (Fig. 6). Let the surface of the layer be parallel to the *x*—*y* plane and let the *z* direction represent a vertical to the layer surface. Fig. 4 shows the behaviour of the electrostatic potential along the *z*-axis for three special verticals to the layer. The chosen verticals represent the positions of the extreme values of the electrostatic potential. All the curves tend to join into a single one above some definite distance from the layer surface. For larger distances the computation of the potential along a single arbitrary vertical is fully sufficient. The studied volume (its edges being 1.0595, 0.9175, and 0.3000 nm in *x*, *y*, and *z* directions, respectively) is represented by a grid of tabulation points, the increments of grid points being 0.0107, 0.0093, and 0.0052 nm in the *x*, *y*, and *z* directions, respectively.

The obtained electrostatic potential enables to estimate the stabilization energy of a cation adsorbed on the surface, the place of the adsorption and also vibrational frequencies of adsorbed ion. The proton can serve as the simplest model cation with pure electrostatic interactions with the partner system. The effect of polarization of the layer caused by the adsorbed proton was assumed to be negligible. Then, the value of the electrostatic potential in its minimum determines the adsorption energy of proton adsorption, ΔH, and the coordinates of the minimum define the position of the adsorbed proton. A sufficiently dense grid of tabulation enables to compute a matrix of the second derivatives of the electrostatic potential in its minimum with satisfactory accuracy. The eigenvalues of this matrix define the force constants of the three modes of vibration of the adsorbed proton and the eigenvectors describe the directions of these three modes in Cartesian representation.

RESULTS AND DISCUSSION

The electrical potential was computed for the grid within the chosen volume as described above. Several chosen cuts and projections, as given in Figs. 5 and 6, give a deeper insight on how the electrical potential behaves near the talc layer. Fig. 5 exhibits the shape of the potential for four parallel planes distant by 0.140, 0.195, 0.265, and 0.325 nm from the talc layer, respectively. As expected, an obvious periodicity in dependence on the periodicity of the structure was observed. The extrema on the potential surfaces have the same *x*—*y* coordinates, just their function values differ. More precise description is illustrated in Fig. 6, where the contour line projection into the *x*—*y* plane for the cut No. 1 (Fig. 5) is plotted. For a better understanding of the relations between the structure of the layer and the behaviour of the potential, positions of the basal oxygen atoms were depicted. The locations of the extrema are seen from this isopotential map.

All minima in the individual *x*—*y* plane cuts are localized atop the basal oxygen atoms. Maxima lie on verticals to the silicate atoms of the tetrahedral sheet. Ellipsoidal shape of minima is caused by the impact of two adjacent silicon atoms. On the other hand, the triangulate shape of maxima results from the impact of three basal oxygen atoms bonded to silicon. Fairly flat maxima localized above centres of hexagonal cavities reflect the presence of OH

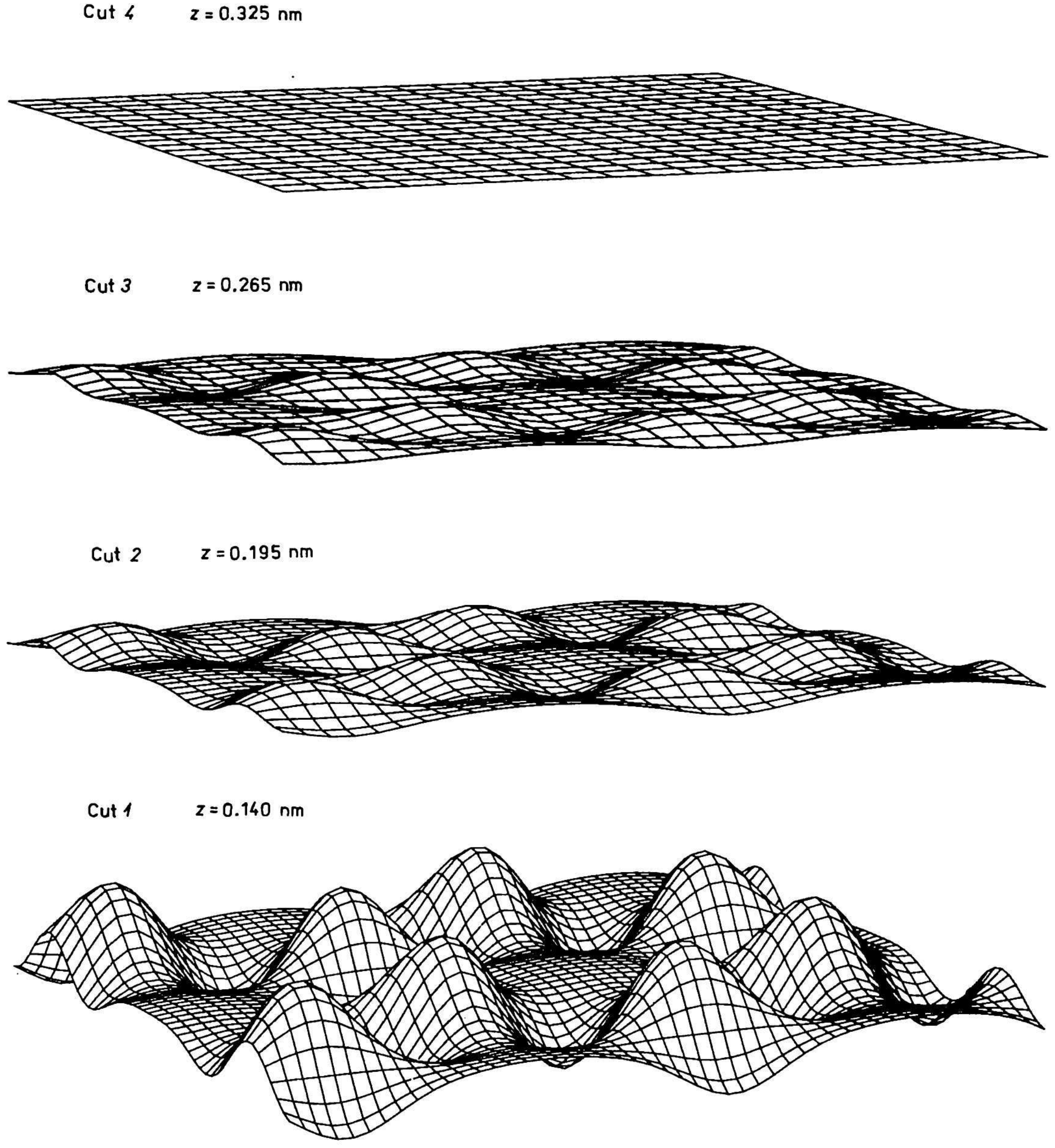

Fig. 5. The electrostatic potential surfaces at the four distances from the talc layer.

groups inside of these cavities. There is also evident another fact from Fig. 5. The electrostatic potential is gradually averaging with the increasing distance from the talc layer. Fig. 4 demonstrates this trend very clearly. The electrostatic potential is drawn as a function of the *z*-coordinate perpendicular to the layer surface in this figure. Three important directions parallel to the *z*-coordinate were chosen: atop the basal oxygens, the silicon atoms, and the hydroxyl groups, respectively. The potential along the vertical to the basal oxygen atoms has significant minimum at z = 0.1095 nm in the value of – 1.09 V. Minima localized above the basal oxygens are the true ones. The other two curves in Fig. 4 have just flat minima at a little larger distance from the layer surface. These minima cannot be the true ones, since the curves connect the maxima in the individual cuts. The potential above the hydroxyl group has also been studied in the interior of the hexagonal cavity (therefore also the negative values of the *z*-coordinate in Fig. 4 are meaningful). At the distance of about 0.3 nm all three curves have tendency to join each other. From that point the potential can be considered to be homogeneous within the given plane cut. Using this assumption, we have fitted the electrostatic potential for the distance greater than 0.3 nm to an exponential function of the form

$$V(z) = C_1 \exp(-C_2 z) \qquad (4)$$

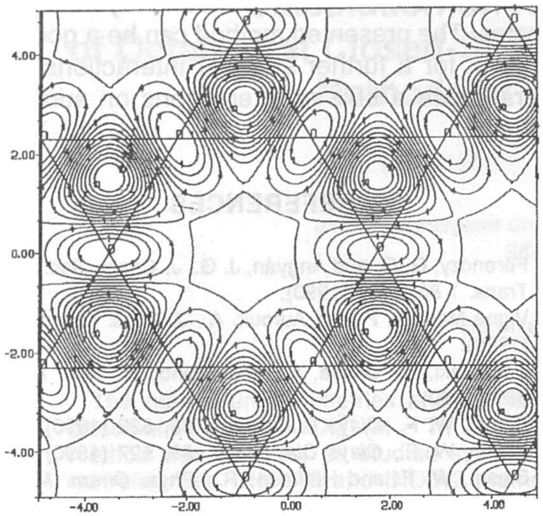

Fig. 6. The isopotential map of the cut *1* from Fig. 4. The contour lines are at the intervals of 0.05 V. (The coordinates are in 10^{-10} m).

The values of C_1, C_2 obtained by the least-squares fitting are: $C_1 = -0.380442$ V, $C_2 = 0.304547$ nm^{-1}, the mean quadratic error being 4.5×10^{-6} V^2.

The potential asymptotically approaches zero with growing distance from the layer, and can be considered as zero for $z > 50$ nm ($V(50) = -9.2 \times 10^{-8}$ V). That means, at least 50 layers from the bulk of a real crystal will contribute to the potential around a crystal surface and will have influence on interaction with some adsorbate on the crystal surface. An interaction among layers in the bulk of the crystal will also be influenced by their environment.

Bleam [5] obtained a different behaviour of the electric potential above the talc layer. Although the positions of extrema obtained in [5] in the *x*—*y* projections were identical with our calculations, the *z* dependence of the potential differs significantly. Agreement in the determination of *x*—*y* coordinates of the extreme points is not surprising due to the structure and symmetry of the layer. Different values and behaviour of the potential along the *z* direction reflect the sensitivity with respect to the used method. *Bleam* [5] used a point-charge model with atomic charges obtained from EHT calculation and the potential reached the zero value for the distance about 0.4 nm from the layer surface. Quantum-chemical calculation of electrostatic potential seems to provide a more realistic description of a charge distribution. Unlike [5], method of calculation of the potential used in the present paper considers the negative charge as delocalized and screening the positive charges from the core of atoms. This fact can also explain the different behaviour of the potential with distance from the layer.

In order to find all extrema appearing in the studied volume, the true extrema have been searched by inspection of the complete grid of computed potential values. Exclusively minima appear at this hypersurface, they are at the distance of 0.1095 nm from the layer surface, and their *x*—*y* coordinates correspond to *x*—*y* coordinates of the basal oxygen atoms. No maxima have been found in the studied volume. All the determined minima are equivalent as far as both their shape and function values are concerned. Positions of these minima are important for the determination of possible places of adsorbed ions as well as a suggestion of possible mutual positions of neighbouring layers. Value of the potential at the minimum determines ΔH of hypothetical adsorption of proton (104.961 kJ mol^{-1}).

Table 1. The Calculated Force Constants, Frequencies and Cartesian Components of the Displacement Eigenvectors of the Three Harmonic Vibrational Modes for Hypothetically Adsorbed Proton (Eigenvectors Correspond to the Minimum with the Coordinates: $x = 0.5886 \times 10^{-10}$ m, $y = 2.4560 \times 10^{-10}$ m, $z = 1.0950 \times 10^{-10}$ m)

Mode	Force constant	Eigenvectors		
$\tilde{\nu}/\text{cm}^{-1}$	J m^{-2}	*x*-Component	*y*-Component	*z*-Component
2311	296.24	0.0118	− 0.1255	0.9921
744	30.72	− 0.8767	0.4758	0.0706
273	4.99	0.4809	0.8705	0.1044

The shape of the potential around the minimum enables to determine force constants of harmonic vibrations for the mentioned proton. Those are eigenvalues of the hessian matrix $[\partial^2 V/\partial \alpha^2]_{(x_{\min}, y_{\min}, z_{\min})}$ of the electrostatic potential at the point of minimum. Table 1 collects eigenvalues of this matrix, corresponding harmonic vibration frequencies, and displacement eigenvectors. These eigenvectors represent directions of the vibrating proton. These directions are the ones of principal axes of vibrational ellipsoid of adsorbed proton. The maximum frequency corresponds to the vibration mode perpendicular to the surface of talc layer. The middle one corresponds to the vibration mode in the direction of a vector connecting silicon atoms, and the lowest frequency also represents the vibration parallel to the layer surface but perpendicular to the Si—Si direction. In spite of the fact that only the electrostatic part of the interaction potential was considered (polarization, dispersion, and repulsion terms were neglected), the obtained vibrational frequencies fell into the interval of the usual frequencies of protons in hydrogen-bonded systems [11].

CONCLUSION

Results obtained in the present study using approximate GP2 method for calculation of the electrostatic potential show that the potential generated by a single layer of talc is a long-range one. The potential for distance greater than 0.3 nm from the layer has the same value over the whole surface of the layer and is asymptotically approaching zero. This part of the potential was fitted by the exponential function.

The positions of minima of the potential were determined by mapping in the studied volume above the talc layer. The energy of hypothetical adsorption of the proton was calculated from the value of the potential in the minimum.

The harmonic frequencies of the three vibrational modes of the adsorbed proton were calculated from the shape of the potential around the minimum. The directions of these vibrational displacements of the proton were determined.

The obtained results, presented in this paper, give a reasonable picture of the electrostatic potential above the talc layer. The symmetry of the layer (including the translational symmetry), and the use of sufficiently large cluster, may be the reason for success of such simplified procedure. However, comparing these results with those obtained by the use of point charge model, it seems that the use of quantum-mechanical computations of electrostatic potentials is the necessary condition for a reliable description of electric fields around layers of phyllosilicates. The presented method can be a good starting point for a further study of interactions among layers inside a bulk or interactions on surfaces of crystals.

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Translated by Š. Varga