

Molecular modelling – opportunities for soil research

Dedicated to Univ. Prof. Dipl.-Ing. Dr. Dr. h.c. mult. Winfried E. H. Blum on the occasion of his 60th birthday

M. H. Gerzabek, A. J. A. Aquino, G. Haberhauer, D. Tunega and H. Lischka

Molekülmodellierung – Perspektiven für die Bodenforschung

Herrn O. Univ. Prof. Dipl.-Ing. Dr. Dr. h.c. mult. Winfried E. H. Blum anlässlich seines 60. Geburtstages gewidmet

1. Introduction

Soil has a large number of functions within the biosphere. Besides of being the basis for crop production, soil acts as one of the main sinks for atmospheric CO₂ and various pollutants. Especially the latter fact is of increasing importance. The soil cover in many cases is the only effective filter and buffer against pollutants entering the food chain. The use of agrochemicals, the application of organic residues containing different organic and inorganic pollutants to agricultural land and immisions of substances originating from combustion processes and regular or accidental releases from nuclear facilities led to a large variety of pollutants already being immobilised in the soil matrix. The main classes of substances of concern are heavy metals, radionuclides, pesticides, hydrocarbons, PAH's, PCB's, dioxins and – more recently under discussion – endocrine disrupters (e.g. GÜLDEN et al., 1997). Especially the number of relevant organic compounds is increasing rapidly and data on the behaviour and fate of these substances are urgently

needed. Thus, the questions we ask in soil science are getting even more complex than a few decades ago, when soil productivity was the main matter of concern. The largest effort in this context is needed to investigate the specific adsorption and fixation processes for a given compound, which comprises the most important basis for the estimation of its environmental behaviour. Laboratory and lysimeter studies (FÜHR et al., 1998; GERZABEK et al., 1998) are the most important methods in this connection. Anyhow, these studies are quite time consuming and may not be readily available for a first quick risk assessment of a new compound being just in development or recently discovered in the environment. Theoretical studies, thus, could be useful to assist the risk assessment and to help understanding the processes of interactions with the soil matrix on a molecular level.

Computational chemistry (CC) is a quite young science and its potential is intimately connected with the capabilities of computer hard- and software (see chapter 2). The rapid increase in computational power available enables

Zusammenfassung

Die Computerchemie (CC) ist eine relativ junge Wissenschaft, die sich rasch entwickelt. Dies hängt auch mit der zunehmenden Leistungsfähigkeit von PCs und Workstations zusammen. Derzeit wird die Computerchemie selten in der bodenkundlichen Forschung verwendet, obwohl zahlreiche Anwendungsgebiete – insbesondere auf dem Gebiet der Erforschung des Verhaltens von Umweltschadstoffen im Boden – vorauszusehen wären. Neue Techniken, wie beispielsweise die ONIOM-Methode ermöglichen in diesem Zusammenhang relativ genaue Berechnungen von Interaktionen auch innerhalb großer Systeme mit bis zu 100 Atomen. Ein weiteres interessantes Forschungsfeld ist die Untersuchung der hypothetischen Struktur von Huminstoffmodellen und von Interaktionen mit verschiedenen Schadstoffen. In der vorliegenden Arbeit werden Beispiele für Anwendungen der Computerchemie in der Bodenforschung präsentiert: (i) die Interaktion von organischen Säuren mit Aluminium, (ii) die hypothetische Struktur von Huminstoffmodellen und deren Wechselwirkung mit Pflanzenschutzmitteln und (iii) die Anwendung der ONIOM Methode für das Studium der Adsorptionsstellen an Tonmineraloberflächen.

Schlagerworte: Aluminium, Bodenforschung, Computerchemie, Huminstoffe, Tonminerale.

Summary

Computational chemistry (CC) is a young science which develops rapidly. This is intimately connected with the increase in computer power and the recent rapid improvement of PCs and work stations. Although at present seldom used, numerous applications in soil science, especially in pollution research, can be envisaged. New techniques as e.g. the ONIOM method make it possible to investigate interactions within quite large systems of up to 100 atoms with high accuracy. Another interesting field for CC are studies of the hypothetical structure of humic substance models. These can be used for investigations of interactions with various pollutants (e.g. "bound residues"). In this paper we exemplify quite different applications of CC in soil research: (i) the interaction of organic acids with aluminium, (ii) the hypothetical structure of humic substances and their interactions with pesticides and (iii) the use of the ONIOM technique to study adsorption sites on clay minerals.

Key words: aluminium, clay minerals, computational chemistry, soil research, humic substances.

more and more accurate calculations and an application to a wider range of systems. Since even personal computers and small workstations nowadays allow to perform modelling calculations if the described systems are not too large, computational chemistry has entered more applied sciences like soil science. Anyhow, these theoretical methods are seldom used in soil science up to now and applications are restricted to a few topics. The potential of CC has been already shown e.g. for studies on Al-organic acid complexes (AQUINO et al., 2000; TUNEGA et al. 2000), for investigations of clay mineral interlayers and their surface geochemistry (CHANG et al., 1998; 1999, SPOSITO et al., 1999) and modelling smaller systems of humic substances (SCHULTEN and SCHNITZER, 1997). Thus, CC is and will be used to investigate soil processes in the micro-scale in the future.

The present paper attempts (i) to review some of the work already been done in soil science with the tool CC and (ii) to give examples of recent studies highlighting the potential of CC methods for future research.

2. Recent developments in computational chemistry

Computational Chemistry is a rapidly growing section of Theoretical Chemistry with emphasis on application-oriented molecular problems being solved on the computer. The fundamental equation determining the properties of atomic and molecular systems is the Schrödinger equation. Its analytic solution is only possible for a few simple model cases. Based on the rapid progress in computer technology, very powerful numerical methods and respective computer programs have been developed for the quantum chemical computation of atoms and molecules. These methods have

been applied very successfully in practically all fields of chemistry. Several classes of computational procedures are available ranging from ab initio and DFT (density functional theory) level via semi-empirical methods to simple force-fields and interatomic potentials. In these series of methods the first two ones are computational most expensive. However, they give on the average the most reliable results. Semi-empirical methods are computationally less expensive, but require well-tuned parameter sets for successful application. Finally, force-field and interatomic potential methods are by far the cheapest ones. They lack any quantum chemical formalism and rely heavily on the empirical adjustment of parameters. From the large number of methods and computational techniques only a few of them, which are directly relevant to our work, will be discussed here. For more information and for an overview of typical applications see e.g. JENSEN (1999).

Sufficient flexibility and reliability of the computational methods are of particular importance in soil sciences, since we have to deal with various types of interactions and chemical bonding such as intermolecular forces between solute and solvent, adsorption processes on surfaces and chemical bonds occurring in the inorganic and organic constituents of the soil. Besides this great variability in the interactions, it is also the size of the individual subsystems, which makes the calculations very time-consuming. For example, the adsorption process on the clay surface requires either the computation of a larger cluster cut out from the crystal structure or the treatment as a periodic system with a large unit cell including the adsorbed species. The humic substances are polymers with a very irregular structure and therefore difficult to describe.

In the present contribution we concentrate on DFT methods. They belong – as has been stated above – to the

most “expensive” ones, but combine the required flexibility and reliability with computational efficiency. Most of the calculations described in this work have been set up as benchmark investigations which shall guide future investigations on even larger and more complex systems.

One of the most crucial practical bottlenecks in an *ab initio* or DFT calculation besides computer time is the huge amount of data produced. This problem has been overcome by the introduction of “direct” methods where storage of these data is avoided by recomputation every time they are needed. This technique is available in all major quantum chemical program packages (e.g. GAUSSIAN98, 1998 or TURBOMOLE (AHLRICHS *et al.*, 1989; ARNIM, 1998)). Several additional techniques have been developed within *ab initio* and DFT approaches, which are especially dedicated to the reduction of the effort required for the computation of larger molecules. One of those is the RI method (VATRAS *et al.*, 1993; EICHKORN *et al.*, 1995) in which the calculation of the most time consuming two-electron integrals is substantially reduced by the introduction of an auxiliary basis set. Using these methods, DFT calculations on fullerenes C_{60} up to C_{80} and inorganic clusters such as $[Cd_{32}Se_{14}(SeH)_{36}(PH_3)_4]$ have been reported (AHLRICHS *et al.*, 1998). Another alternative for the calculation of large molecules is the ONIOM method (DAPPRICH *et al.*, 1999). The basic idea of this method is the partitioning of the entire system in two or more layers, where the important part (inner layer) is treated at a higher level of theory and the remaining layers at lower levels. In total, calculation of molecules with 100 atoms or more are feasible nowadays. Many of these calculations can be carried out even on standard PCs under Linux, which provides a very cost-effective alternative to high-end workstations or central computers.

Solvation effects play a crucial role in soil processes. The inclusion of solvation poses very challenging problems for quantum chemical calculations. One conceptually simple approach is the embedding of the solute molecule into a cluster of solvent molecules and to treat the whole system as a supermolecule. However, if the solute is polar or even charged, strong and far-reaching interactions between the solute and solvent molecules will occur. In order to accommodate for these extended interactions, very large clusters of solvent molecules would have to be taken into account, which increases the cost for the computation drastically. Therefore, continuum solvation models have been developed, which provide a good and cost-effective alternative. In this approach the solute (eventually together with a first solvation sphere) is embedded into a polarisable dielec-

tricum. Early continuum models (BORN, 1920; ONSAGER, 1936; KIRKWOOD, 1935) were of limited value for quantitative predictions due to the intrinsic simplicity of these models. In the pioneering work of MIERTUS *et al.* (1981) the polarisable continuum model (PCM) was developed which is now together with the SCRF (self-consistent reaction field) method the basis for most of the recent computer implementations (TOMASI and PERSICO, 1994). In the PCM model the solute molecule is placed into a cavity created within the continuum. This cavity is constructed by means of overlapping spheres centered on the atoms of the solute, which allows a realistic description of the shape of the molecule. The electrostatic potential of the solvent is represented as point charges at the surface of the cavity. The quantum chemical part of the calculation includes the nuclear charges and electrons of the solute molecule and the point charges describing the continuum. The mutual polarization between solute and solvent is taken into account by the aforementioned SCRF method.

3. Examples for applications of computational chemistry in soil science

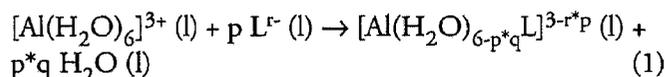
3.1. Interaction of aluminium with organic acids – a theoretical study

The aluminium cation plays an important role in soil chemistry. Free forms (e.g. as hexaaquo complex) present toxicological risks for organisms and especially agricultural crops and affect the quality of natural sources of water. Organic acids occurring in the soil have strong influence on the chemical activity of aluminium. Formation of various stable complexes can decrease negative factors of the occurrence of aluminium in soil. Thus, it is important to understand the related chemical processes in more detail in order to develop better strategies for the deactivation of free aluminium. The formation of complexes between aluminium and organic acids has been investigated extensively, mainly based on studies of dissolution processes of aluminium-containing minerals (see e.g. PALMER and BELL, 1994; FEIN and HESTRIN, 1994). The analysis of these measurements in terms of stabilities of individual compounds is complicated by the fact that a large number of coupled chemical equilibria occur in solution. Their resolution yields good global information on different groups of complexes but does not give details about the structures involved. Quantum chemical methods can be used to obtain such detailed

informations. Such investigations have, e.g. been carried out on several complexes between aluminium and organic acids by KUBICKI et al. (1996, 1999).

The aluminium cation has an amphoteric character. This means that the pH of the solution will have a strong influence on the question which complexes will be formed. We focused on complexes where aluminium is sixfold coordinated which is characteristic for a pH below 7. At such conditions organic acids exist in aqueous solution in dissociated form. Thus, aluminium can form complexes in aqueous solution with fully or partially deprotonated organic acids, hydroxyl anions and with water molecules. A typical complex structure can be characterised by the formula $\text{Al}(\text{H}_2\text{O})_p(\text{OH})_q\text{L}_r$, where L_r stands for a deprotonated acid as ligand. In our theoretical investigations (TUNEGA et al., 2000; AQUINO et al., 2000) we restricted ourselves to complexes without OH^- group in the Al^{3+} coordination sphere. The studied species were complexes with the acetate and oxalate anions ($\text{L} = \text{Ac}^-$ and Ox^{2-}) as ligands. The bonding links from these ligands to aluminium are the oxygen atoms from the carboxylate groups. Bonding can occur in monodentate and bidentate form (see examples given in Fig. 1a and 1b). Since Al^{3+} possesses a sixfold coordination sphere, complexes with several ligands are possible. Moreover, in the case of complexes with two acetate or two oxalate anions *cis*- and *trans*- isomers can be formed. The calculations have been carried out at the DFT level using the PCM model for the inclusion of solvent effects. The quantum-chemical calculations were performed with the GAUSSIAN98 package. The BLYP density functional method and a split valence polarization (SVP) basis set augmented with diffuse *s* and *p* functions on the oxygen and carbon atoms (SVP+*sp*) were used in all calculations. For the relative dielectric constant ϵ the value of 78.54 of water was chosen. All thermodynamic data have been evaluated for a temperature $T = 298.15$ K. For more information on technical details see TUNEGA et al. (2000) and AQUINO et al. (2000).

The following complexation reactions have been studied:



where *p* is the number of ligands (*p* = 1, 2, 3) and *q* = 1 or 2 for mono- and bidentate ligands, respectively. In Table 1 solvation energies E_{solv} , reaction enthalpies ΔH_r and Gibbs free reaction energies ΔG_r are given according to Eq. 1 for the most stable aluminium-acetate and aluminium-oxalate complexes. One can see that solvation energies are very large

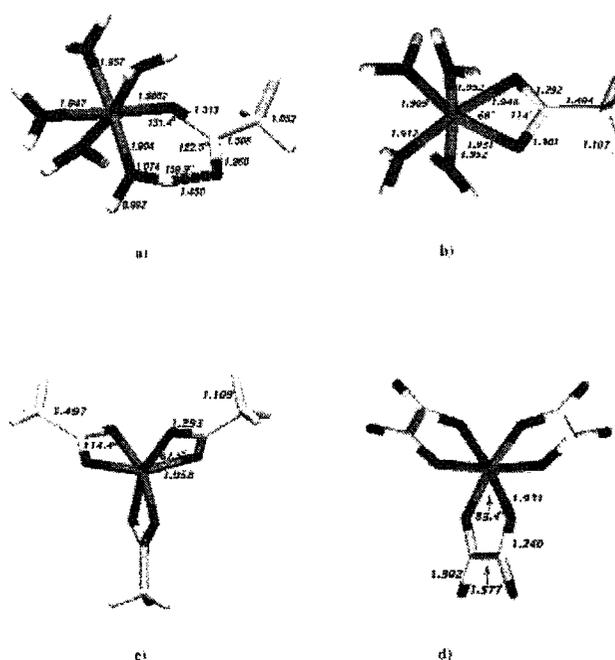


Figure 1: Optimized BLYP/SVP+*sp* geometries for water as solvent –
 a) monodentate- $[\text{Al}(\text{H}_2\text{O})_5\text{Ac}]^{2+}$
 b) bidentate- $[\text{Al}(\text{H}_2\text{O})_4\text{Ac}]^{2+}$
 c) bidentate- AlAc_3
 d) bidentate- $[\text{AlOx}_3]^{3-}$

Abbildung 1: Optimierte BLYP/SVP+*sp* Geometrien für Wasser als Lösungsmittel –
 a) monodentates $[\text{Al}(\text{H}_2\text{O})_5\text{Ac}]^{2+}$
 b) bidentates $[\text{Al}(\text{H}_2\text{O})_4\text{Ac}]^{2+}$
 c) bidentates AlAc_3
 d) bidentates $[\text{AlOx}_3]^{3-}$

in absolute values. As expected, the solvent effect is proportional to the total charge of the system. For example, the solvent energy of the hexaquo complex $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ is -467.5 kcal/mol while for the $[\text{AlAc}_3]^0$ it is only -4.1 kcal/mol. In general, the size of the solvation energy of the complexes between aluminium and the organic acids will depend heavily on the amount of charge compensation which takes place when the complex is formed. This strong variation in solvation energies of the individual species has, of course, also a significant influence on the overall solvent effect for the reactions given by Eq. (1).

Comparing $\Delta H_r(\text{l})$ values in Table 1 it is found that the most stable complexes in each set (acetate or oxalate) are those where the water molecules in the hexaquo complex are fully replaced by the organic acid ligands. The oxalate complexes are in general more stable than the acetate complexes. While bidentate acetate complexes are less stable than monodentate

Table 1: Calculated solvent energies, reaction enthalpies and reaction Gibbs free energies (Eq.1) at the B3LYP/SVP+*sp* level for aluminium-acetate and -oxalate complexes, respectively (All energies are in kcal/mol)

Tabelle 1: Berechnete Lösungsenergien, Reaktionsenthalpien und Gibbs'sche Reaktionsenergien (Gl. 1) berechnet auf dem B3LYP/SVP+*sp* Niveau für Aluminium-Azetat bzw. Aluminium-Oxalat Komplexe (alle Energien in kcal/mol)

Complex	E_{solv}	ΔH_r (l)	ΔG_r (l)
m-[Al(H ₂ O) ₅ Ac] ²⁺	-198.2	5.2	3.5
b-[Al(H ₂ O) ₄ Ac] ²⁺	-204.1	15.9	8.1
m-[Al(H ₂ O) ₄ Ac ₂] ⁺ - <i>cis</i>	-59.7	-15.3	-11.9
b-[Al(H ₂ O) ₂ Ac ₂] ⁺ - <i>cis</i>	-59.9	6.8	-11.7
b-[AlAc ₃] ⁰	-4.1	-4.9	-28.2
m-[Al(H ₂ O) ₅ Ox] ⁺	-100.9	9.8	8.7
b-[Al(H ₂ O) ₄ Ox] ⁺	-107.5	5.6	-6.3
b-[Al(H ₂ O) ₂ Ox ₂] ⁻	-80.6	-9.4	-31.7
b-[AlOx ₃] ³⁻	-335.0	-20.1	-47.4

ones according to ΔH_r , for oxalate complexes the situation is reversed (cf. the pair of the first/second and the sixth/seventh rows in Table 1). The reason for this behaviour comes from the fact that in the acetate case only one carboxylate group is involved in the bidentate binding whereas it is two different carboxylate groups in case of oxalate. Characteristic differences between ΔH_r and ΔG_r are observed for mono- and bidentate complexes. Reactions with bidentate structures are significantly enhanced at the ΔG_r level. In case of acetate ligands the formation of bidentate complexes becomes almost equivalent to that of the monodentate species. For oxalate complexes the difference between the formation of mono- and bidentate structures becomes even more favourable for the latter. The differences between ΔH_r and ΔG_r are relatively small for the formation of monodentate species (e.g. 1.7 kcal/mol for monodentate [Al(H₂O)₅Ac]²⁺) but much larger for bidentate cases (e.g. 7.8 kcal/mol for bidentate [Al(H₂O)₄Ac]²⁺). A detailed analysis performed by AQUINO et al. (2000) showed that the reason for this behaviour is the increase in entropy because of the additional number of water molecules released from the aluminium coordination sphere after substitution by a bidentate ligand as compared to a monodentate one. Therefore, it was concluded that reactions for monodentate complexes are energy-driven, whereas those for the bidentate complexes are entropy-driven.

Experimentally determined ΔG_r values were -3.8 kcal/mol and -6.2 kcal/mol for the AlAc²⁺ and AlAc₂⁺ complexes (PALMER and BELL, 1994) and -15.5, -18.2 and -19.6 kcal/mol for the AlOx⁺, AlOx₂⁻ and AlOx₃³⁻ complexes (FEIN and HESTRIN, 1994). In both experimental investigations

only global chemical reactions of the type $\text{Al}^{3+} + m\text{L}^n \rightarrow \text{AlL}_m^{3-m*n}$ were taken as basis and no details of the coordination sphere of Al³⁺ such as the number of water molecules or other ligands were specified. Moreover, it is not possible to distinguish mono- and bidentate structures from the experimental data. In view of this situation we have found relatively good agreement with experimental values and our predictions of the most stable complexes agrees with experimental observations.

3.2. Hypothetical structures of humic substances and modelling of interactions of soil organic matter with pesticides

Humic substances as a very stable and reactive part of soil organic matter play a crucial role in the fate and behaviour of organic pollutants and heavy metals in the environment. Adsorption of organic contaminants or heavy metals onto soil organic matter has the potential to be a major controlling factor in their bioavailability. Models for estimating the amount and stability of sorbed contaminants based simply on the fraction of organic carbon in a soil can oversimplify the process of sorption in the environment. It was shown that origin, structural characteristic and/or interaction of HS with clay minerals affect the sorption behaviour. In order to help to understand sorption processes, several models of soil organic matter components, which are possible substrates for sorption, have been developed on a molecular level.

Molecular modelling of humic substances is restricted due to the availability of structural information. Experimental models, based on breaking down humic substances through pyrolysis (SCHNITZER and SCHULTEN, 1992) or thermochemolysis (DEL RIO and HATCHER, 1996) and the determination of the formed components were generated. The analysed fragments are used to rebuild the overall structure. However, both side reactions during the pyrolysis process and the lack of information how these fragments are linked together limit the use of this information to create two dimensional models of humics. Infrared spectroscopy and NMR spectroscopy supplies information on an approximate distribution of functional groups within humic acids. Together with these IR, NMR, UV data, mass spectrometry results using soft ionisation techniques, like MALDI-TOF MS or ESI-MS, demonstrate the complexity of humics (HABERHAUER et al., 1999; BROWN and RICE, 2000; SOLOULKI et al., 1999). Thus, humic substances, which can be assumed to be complex mixtures of com-

pounds with no prevailing single molecule, present a challenging task for modelling.

2-dimensional models

In order to visualise interactions of humic substances (HS) with other molecules two dimensional models were developed. Such representations were constructed using the existing limited structural information. So, it is always important to keep in mind that such models are only an approximation to illustrate selected processes and that these models can not reflect the whole complex properties of humic acids. Such two dimensional models were proposed by many authors and many of them are now used in textbooks (e.g. SCHACHTSCHABEL et al., 1989). Two dimensional models can be used to visualise and graphically describe interactions between organic matter and pollutants or clay minerals. A possible example of such a model is shown in figure 1. According to average structural data this model is composed of aromatic, lipophilic aliphatic, polar and carboxylic moieties. Several two dimensional models were published in the last ten years. Some consist of macromolecules (SCHNITZER and SCHULTEN, 1992) or polymerizable units (DAVIS et al., 1997) while other models propose that humic acids are crude mixtures of low molecular weight compounds (STRUMPF, 1998). However, all

models have in common that few scientific structural prove exists for any of the proposed constitutions.

3-dimensional humic substance models

A two dimensional presentation of structures does not allow to understand and visualise many types of interactions between molecules. Three dimensional representations are necessary to describe complex reactions in biological systems. Therefore, a demand of suitable three dimensional humic substance models exists in order to describe several types of adsorption processes. In case of interactions of clay materials and organic compounds some recently published papers demonstrate the suitability of computational chemistry methods (SPOSITO et al., 1999; PARK et al., 1997; CHANG et al., 1997). Molecular dynamic methods were employed to examine sorption behaviour of organic compounds in clay interfacial structures (TEPPEN et al., 1998). The availability of clay mineral structures and molecular structures of the investigated organic compounds enables comparison of the theoretical data to experimental results. The fast development of computational chemistry and understanding of structural requirements allow the construction and modelling of three dimensional models out of two dimensional concepts (Figure 2). Three dimensional construction of humic substance models using several types

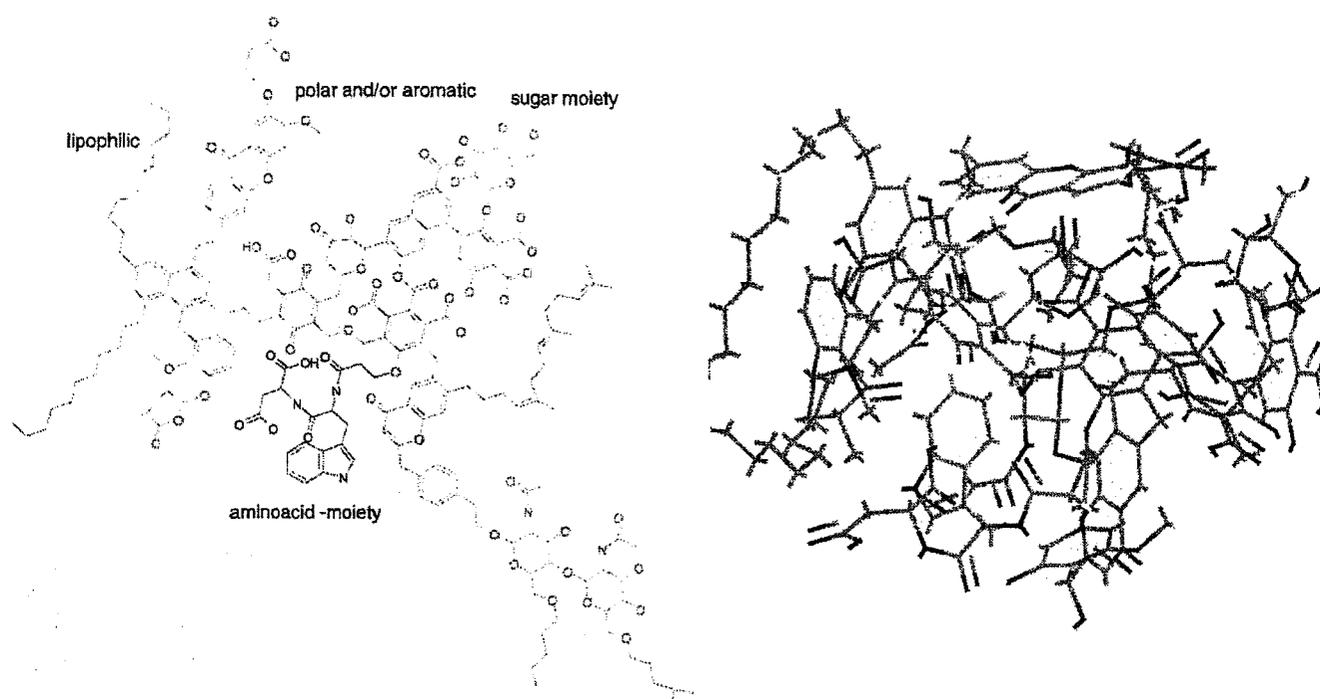


Figure 2: Two (left) and three (right) dimensional graphical representation of a hypothetical humic substance model
Abbildung 2: Zwei (links)- und dreidimensionale(rechts) graphische Darstellung eines hypothetischen Huminstoffmodells

of available molecular modelling software packages and subsequent minimisation of the structures using force field or semi empirical methods will generate stable conformations (see Figure 2 and SCHULTEN and SCHNITZER, 1995). SCHNITZER and SCHULTEN (1997) used molecular modelling programs to build a humic substance model using their two dimensional concept. SEIN et al. (1999) investigated the conformational flexibility of their humic substance building block. Three dimensional structures of HS were used to describe (SCHULTEN, 1996; SCHULTEN, 1999; SCHULTEN and LEINWEBER, 2000) and illustrate (VON WANDRUSZKA, 1998) the interaction with xenobiotic compounds. Strong H-bonding was predicted to play an important role within the formation of humics and organic compounds complexes (KUBICKI and APITZ, 1999).

Even if the use of computational chemistry in that respect seems to be very attractive there are several limitations regarding this humic substance representation approach. First, one of the most serious limitations for the application and relation of such studies to environmental processes is the lack of structural support for the chosen two dimensional models. Second, it is questionable if folding of such macromolecules (In many cases minimisation was used for 2 D to 3D transformation) will give any realistic results. Even if modern computational methods are used the modelling of folding of well characterised macromolecules such as proteins (SOCCI et al., 1998) is restricted by many parameters. Third, the conformational space of flexible macromolecules allows a huge number of different conformations. Identification of the environmental important conformations requires at least some basic structural data (LEACH, 1996). Additionally, the used force fields are often not optimised to study organic – cation or organic mineral bonding. Both bonding types are of great importance in soil environments. Thus, the adaptation and development of force fields for such interactions should be considered.

Macromolecular models were used for the description of single interactions (e.g. H-bonding) in a defined environment (= conformation/structure of humics), but due to the lack of conformational and structural data no direct relation of the output to experimental results can be gained. In order to circumvent these problems other approaches were chosen to describe the interaction of humic substance moieties to organic compounds.

Reductive approaches of the description of humic substances

Therefore, one of the first approaches to model humic substances were based on meso-size models. These models con-

sist of hydrophilic and hydrophobic parts and can be used to describe the amphoteric and surface active behaviour of humics. In comparison to molecular models these so called secondary structural models of humic materials (WERSHAW et al., 1986) are directly developed from experimental results and used to explain certain behaviour of humics. Therefore, less arbitrary assumptions are necessary to create them. Such models can be utilised to describe the built up and the formation of humics in soil and aqueous environments. They have brought an important input in our nowadays understanding of humic substances (CONTE and PICCOLO, 1999; WERSHAW, 1993). Another approach applying computer modelling to structural problems of humics without describing the complete molecular structure was chosen by BIRKETT et al. (1997). The authors commenced their modelling defining humics by a set of groups and not on an atomic level. Humic substances are represented by the molecular volume, amount of carboxylic, aromatic and several other groups. The average group information can be directly obtained from experiments. Information on how these groups are connected and how humic molecules are constituted (data which are not total available) are not required. Therefore, in comparison to the molecular structural models no additional assumptions have to be made.

However, both above mentioned conceptional approaches on a meso-scale do not allow to model or describe interactions between small organic molecules such as pesticides or various organic pollutants and humic substances on an atomic level. Models, which consist of functional moieties of humic substances only, can be used to describe sorption strength of different sorptive sites (KUBICKI and APITZ, 1999). Such models rely on experimental structural information. Additionally, the small size of the models – they contain mainly less than 100 atoms – allows the use of precise quantum chemical methods. Thermodynamic data can be obtained using such methods. These theoretical results could be related to experimental data (TUNEGA et al., 2000). The application of self-consistent field methods mimics solvation or hydrophobic environments (KUBICKI et al., 1999). Thus both single interactions in hydrated and non hydrated environments can be examined. However, since sorption of organic compounds in soil is governed by several different binding sites, a number of possible interaction types must be considered. Quantum chemical calculations were used for rough estimations of possible interaction energies of a herbicide with mineral or soil organic matter moieties (HABERHAUER et al., 2000a). The systems investigated consist of either a mineral moiety, which can be

regarded as a model for a mineral surface edge, or/and an organic molecule representing a structural moiety of soil organic matter and the herbicide. The calculations pronounced the importance of several types of polar interactions and are in agreement with the experimental results.

Another application of computational chemistry to soil sorption processes is the relation of the experimentally determined adsorption directly to the structures of the compounds investigated. Structural parameters, such as size, polarity or/and charge distribution can be compared to adsorption and desorption data of a group of structurally similar compounds (HABERHAUER et al., 2000b). The information on chemical structures was used to estimate soil partition coefficients (LOHNINGER, 1994). Modification in structure can effect the sorption behaviour and could be used for the interpretation of sorption mechanism of a group of structurally similar organic compounds.

3.3. ONIOM study of adsorption sites on the 001 surface of 1:1 clay minerals

Clay minerals represent an important inorganic component of soils and significantly affect physicochemical processes therein. Clays are usually small powder particles (< 2 mm) with a high specific surface area and a high chemical surface activity. Adsorption of mobile chemical species from soil solution on mineral surfaces is a very important process occurring in soil. Soil solutions represent chemically very complex systems containing inorganic ions and organic molecular species originated from natural biochemical processes or from human activities. Especially the behaviour of pollutants in soil (radionuclides, heavy metals, pesticides etc.) is – due to their potential adverse effects on the ecosystem – the main focus of many investigations (SCHACHTSCHABEL et al., 1989). Among organic species, acids and their derivatives play an important role because of the relatively high chemical activity of their carboxyl groups. Organic acids affect the pH of soils and can also strongly interact with other compounds in solution forming various associates and complexes, or with the surfaces of the inorganic/organic solids forming strongly bound adsorbates. Experimentally, it is very difficult to distinguish energetically different adsorption sites on mineral surfaces (e.g. between “regular” 001 surfaces and edge surfaces (110, 010) with broken bonds) or to extract side effects accompanying adsorption (like formation of complexes or intercalations).

Computer simulation methods are very useful for the

detailed description of interactions of molecular species with clay minerals. Conventional molecular dynamic or Monte Carlo methods based on classical force fields have been used in the study of interaction of water or small organic compounds on clay mineral surfaces or inside of the interlayer space (DELVILLE, 1995; BRIDGEMAN and SKIPPER, 1997; TEPPEN et al., 1998; SHROLL and SMITH, 1999; SMIRNOV and BOUGEARD, 1999). A disadvantage of those methods is the difficulty to determine a balanced set of parameters for the empirical potentials, mainly for the interactions between different kinds of atoms in the clay and in the adsorbed molecules. Periodic *ab initio* total energy pseudopotential calculations were performed on the talc-water and pyrophyllite-water systems (BRIDGEMAN et al., 1996). A molecular cluster approach can also be used in studies of the interactions of small molecular species with clay mineral surfaces. In this approach only a certain fragment of the solid-state structure is treated. Only a very few papers (CHATTERJEE et al., 1997; ZHANPEISOV et al., 1999; PELMENSCHIKOV and LESZCZYNSKI, 1999) have been published on molecular clusters which were realistically describing a clay layer structure using an *ab initio* molecular orbital approach. Such cluster models would contain about fifty atoms and more, which implies a computationally very demanding task within the *ab initio* or DFT framework. The aim of the present work was the study of the interaction of water, acetic acid and acetate with different adsorption sites of the 001 surface of minerals of kaolinite-type applying the cluster model approach together with the ONIOM layer technique (DAPPRICH et al., 1999). These model systems represent the basis for future investigations of pesticide-clay interactions.

One individual layer of kaolinite consists of two connected sheets – a tetrahedral sheet formed from corners sharing SiO_4 tetrahedra and an octahedral sheet consisting of edges sharing AlO_6 tetrahedra. Both sheets have a common plane of apical oxygen atoms. One third of all possible octahedral central positions are empty. This creates cavities in the octahedral sheet and also causes deformation of the other octahedra. Hydroxyl groups participating in hydrogen bonds with basal oxygen atoms from adjacent layers cover the outer surface of the octahedral sheet. The tetrahedral side of the single layer has characteristic ditrigonal cavities and the surface is formed from the plane of basal oxygen atoms each shared by two silicon atoms. These two planes (tetrahedral basal oxygen atoms and octahedral surface hydroxyls) are parallel to the crystallographic 001 surface and can be considered as electronically saturated. Each of these two planes forms an important part of the surface of the macroscopic mineral particle.

The cluster model of the single kaolinite layer was derived from the structure of the mineral dickite (JOSWIG and DRITS, 1986). It consists of 78 atoms and contains one ditrigonal tetrahedral ring and one octahedral ring. Dangling bonds were saturated with hydrogen atoms. The structure of this layer fragment can be seen in Figures 3-6. The adsorbants were placed above holes on both sides of the layer – water and acetic acid (HAc) above the tetrahedral side and water and acetate anion (Ac^-) above the octahedral side. The two-layered ONIOM method implemented in the GAUSSIAN98 package was used for all studied systems. In case of adsorption on the tetrahedral side the inner ONIOM layer is the tetrahedral sheet, and in case of adsorption on the octahedral side it is the octahedral sheet. The B3LYP/SVP method was used in all ONIOM geometry optimisation calculations for the inner part and the semiempirical PM3 method for the outer layer. Partial geometry optimisation was performed with the following constraints: the position of the adsorbate with respect to the clay surface and its geometry were fully optimised. The positions of atoms within the clay cluster were kept fixed at the experimental geometry of dickite in order to reduce any artefacts due to finite cluster sizes induced by the geometry optimization. Only the six nearest neighbour hydroxyl groups in case of adsorption on the octahedral side were optimised also. For the optimised geometries single point calculations replacing the PM3 method by MNDO in the ONIOM approach and extending the SVP basis to SVP+*sp* (similar to the aluminium complexes) on atoms (except hydrogen) directly involved in the adsorbent-adsorbate binding were performed. Additionally, the quality of the ONIOM approximation was controlled by performing B3LYP calculations for the whole complex. Interactions energies were corrected to the basis set superposition error (BSSE) according to the counterpoise method of BOYS and BERNARDI (1970).

In Table 2 calculated results for all studied systems are dis-

played. Figures 3-6 present optimised geometries and also contain the most important geometrical parameters.

The D(O)-H₂O system (Figure 3). The water is located above the centre of the octahedral cavity and forms hydrogen bonds with the three surface hydroxyl groups surrounding the empty octahedral hole. It is oriented such that the lone pairs of the oxygen atoms are involved in hydrogen bonds with two surface hydroxyl groups and one proton of the water molecule shows towards one oxygen atom of a surface hydroxyl group. Calculated interaction energies (Table 2) do not differ much between individual methods. Only a small difference is observed between ONIOM and the full approach. More important is the extension of the SVP basis set to the SVP+*sp* quality. The difference between B3LYP/SVP and B3LYP/SVP+*sp* is 2.2 kcal/mol which amounts to about 25% of the B3LYP/SVP energy.

The D(O)-Ac system (Figure 4). The acetate anion is also positioned above the empty octahedral hole. The C-C bond is almost perpendicular to the hydroxyl surface of the layer with the methyl group pointed away from the surface. Both oxygen atoms of the carboxylate group are involved in hydrogen bonding with the four adjacent surface hydroxyl

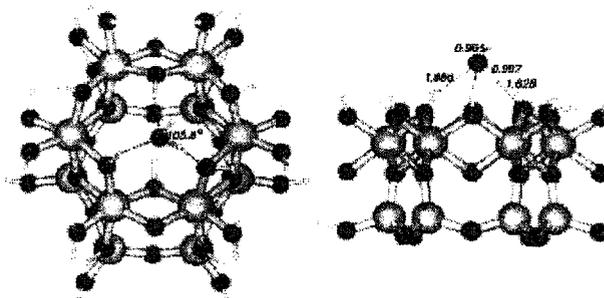


Figure 3: Dickite (octahedral)-H₂O system: ONIOM(B3LYP/SVP: PM3) optimised geometry. Top(left) and side(right) view
Abbildung 3: Das Dickit (oktahedral)- H₂O System: ONIOM(B3LYP/SVP:PM3) optimierte Geometrie. Aufsicht (links) und Seitenansicht (rechts)

Table 2: Calculated interaction energies of water, acetate and acetic acid with the dickite 001 surface (All energies are in kcal/mol)

Tabelle 2: Berechnete Wechselwirkungsenergien von Wasser, Azetat und Essigsäure mit der Dickit 001 Oberfläche (alle Energien in kcal/mol)

System	ONIOM (B3LYP/SVP: MNDO)	B3LYP/SVP	ONIOM (B3LYP/SVP+ <i>sp</i> : MNDO)	B3LYP/SVP+ <i>sp</i>
D(O)-H ₂ O ^a	-10.02	-10.47	-7.17	-8.29
D(O)-Ac ^b	-73.00	-70.08	-69.67	-67.13
D(T)-H ₂ O ^c	-4.51	-3.82	-4.73	-4.14
D(T)-HAc ^d	-2.92	-2.64	-4.06	-2.79

^a Dickite(octahedral side)-H₂O; ^b Dickite(octahedral side)-Ac; ^c Dickite(tetrahedral side)-H₂O; ^d Dickite(tetrahedral side)-HAc

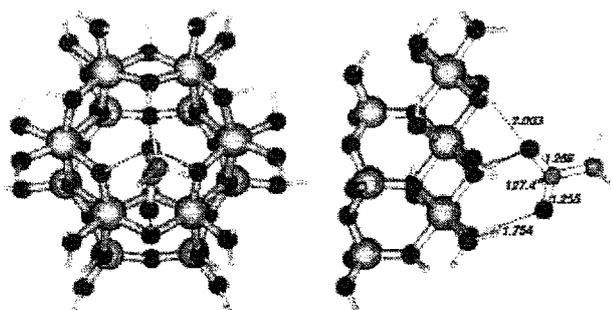


Figure 4: Dickite (octahedral)-Ac⁻ system. ONIOM(B3LYP/SVP:PM3) optimised geometry. Top(left) and side(right) view
 Abbildung 4: Das Dickit (oktahedral)- Ac⁻ System: ONIOM(B3LYP/SVP:PM3) optimierte Geometrie. Aufsicht (links) und Seitenansicht (rechts)

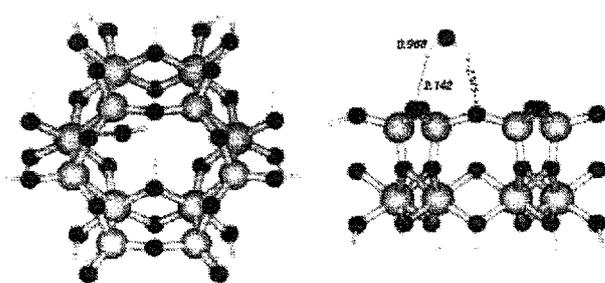


Figure 5: Dickite (tetrahedral)-H₂O system. ONIOM(B3LYP/SVP:PM3) optimised geometry. Top(left) and side(right) view
 Abbildung 5: Das Dickit (tetrahedral)- H₂O System: ONIOM (B3LYP/SVP:PM3) optimierte Geometrie. Aufsicht (links) und Seitenansicht (rechts)

groups. Three bond lengths of the hydrogen bridges are ~ 1.75 Å while the fourth one is much larger (~ 2.00 Å). The interaction energies are much bigger (in absolute value) than those for the D(O)-H₂O system because of the net charge of the acetate anion. As in the previous case, the ONIOM approximation has only a small influence. The relative difference between B3LYP/SVP and B3LYP/SVP+*sp* energies are even smaller (about 9 %) than before.

The D(T)-H₂O system (Figure 5). The water molecule is not located directly above the centre of the ditrigonal tetrahedral hole but is shifted to the side of the ditrigonal ring to form a better contact with two neighbouring oxygen atoms in that ring. The water molecule is oriented with the hydrogen atoms directed towards the basal oxygen atoms and the H-H vector is almost parallel to the plane of these oxygen atoms. The distances between the protons and the contacting oxygen atoms are 2.142 Å and 2.515 Å, respectively. This large bond distances indicate weaker interaction than in the D(O)-H₂O case. Calculated interaction energies (Table 2) vary within one kcal/mol. The average value is about -4.2 kcal/mol. As in the previous cases ONIOM energies do not differ substantially from the full benchmark calculations.

The D(T)-HAc system (Figure 6). The interaction of the acetic acid molecule with the tetrahedral surface is very similar to the previous case. The molecule is positioned almost directly above the centre of the ditrigonal hole and forms one weak hydrogen bond with one basal oxygen atom with a bond length of 1.940 Å. The calculated interaction energies are slightly lower (in the absolute value) than those for the system D(T)-H₂O. The variation in interaction energies between different methods is also similar to the previous case.

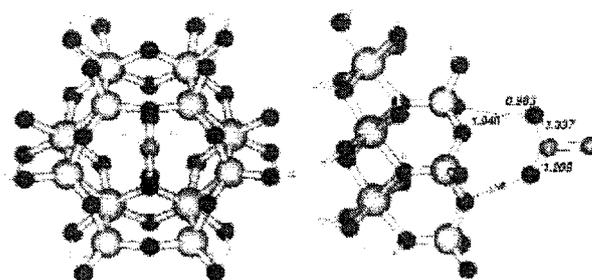


Figure 6: Dickite (tetrahedral)-HAc system. ONIOM(B3LYP/SVP:PM3) optimised geometry. Top(left) and side(right) view
 Abbildung 6: Das Dickit (tetrahedral)- HAc System: ONIOM(B3LYP/SVP:PM3) optimierte Geometrie. Aufsicht (links) und Seitenansicht (rechts)

From the calculated interaction energies it is clear that the two 001 surfaces (octahedral and tetrahedral) of the 1:1 kaolinite layer differ significantly. The tetrahedral side forms only weak hydrogen bonds (energies about -4 kcal/mol for water and acetic acid, respectively). On the other hand, the octahedral side covered by hydroxyl groups is involved in the relatively strong hydrogen bonds (about -8 kcal/mol for water) as one can see also from the shorter respective bond distances. Figure 3 also shows that one water molecule has more possibilities to form hydrogen bonds on the octahedral side than on the tetrahedral one (see Fig. 5). They are even stronger because of cooperative effects. The ONIOM approach turned out to be a powerful and effective method for investigations of the interactions of relatively large molecular systems interacting with clay mineral surfaces.

4. Conclusions

Based on the reviewed literature it may be summarized that computational chemistry is an emerging science within soil research. Interesting examples of its application were already presented in literature, especially in the field of structural investigations of solid soil constituents.

The studies presented in this paper support that:

- interactions of small molecules (Al-acetate, Al-oxalate) can be calculated by DFT-methods with relatively high accuracy
- different humic substance models as basis for further investigations can be derived by molecular modelling methods based on structural information provided by various analytical investigations
- linking molecular structural information of organic pollutants to their adsorption behaviour in soil might provide new insights in sorption mechanisms
- the development of cluster models seems to be a promising way for the investigation of molecular interactions in larger systems like the clay mineral/soil water interface.

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Addresses of authors

Univ. Prof. D.I. Dr. Martin H. Gerzabek, D.I. Dr. Georg Haberhauer, Department of Environmental Research, Austrian Research Center Seibersdorf, A-2444 Seibersdorf; e-mail: martin.gerzabek@arcs.ac.at

Univ. Prof. Dr. Hans Lischka, Institute for Theoretical Chemistry and Structural Biology, University of Vienna, Währingerstrasse 17, A-1090 Vienna;

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