



# A Novel Approach to the Solvation of Methane in Water



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## Introduction

The standard model for the formation of gas hydrates (van der Waals and Platteeuw, 1959) assumes a preformed water/hydrate lattice, into which the methane molecules adsorb [1].

The average lifetime of a water cluster in liquid water is too short to justify the assumption of a preformed hydrate lattice. Our aim is the development of an alternative model for the gas hydrate formation starting from  $\text{CH}_4@(\text{H}_2\text{O})_{20}$  clusters, since the dodecahedra in the different gas hydrates are very similar to the solvation shell of methane in liquid water. We assume further, that the hydrate lattice is formed then by the coagulation of these clusters.

## Model development

Since our model is going to base on  $\text{CH}_4@(\text{H}_2\text{O})_{20}$  units, an accurate description of these clusters is essential for the success of the future model. The common quantum chemical approach to such a problem starts from high level quantum calculations of small methane-water clusters, which are then used to analyse the solvation mechanism in various ways.

It has been suggested in literature [2], that multicenter effects within the hydrogen bond framework have an significant influence on the methane-water interaction energy. To circumvent the problems caused by any cut through the  $\text{CH}_4@(\text{H}_2\text{O})_{20}$  cluster, we start our calculations with the whole  $\text{CH}_4@(\text{H}_2\text{O})_{20}$  unit.

Our super molecular approach is based on a cluster, which describes the first solvation shell of the methane molecule. The geometry of our model bases on the following assumptions, which were derived from a transformation of the ice-rules by Bernal-Fowler-Pauling.

- methane is positioned exact in the cluster center
- water molecules are positioned on the vertices of a regular dodecahedron
- each water molecule is nearly tetrahedral coordinated. Three of the coordination sites are occupied with other water molecules from the cluster
- each water molecule has six possible orientations (see figure 1)

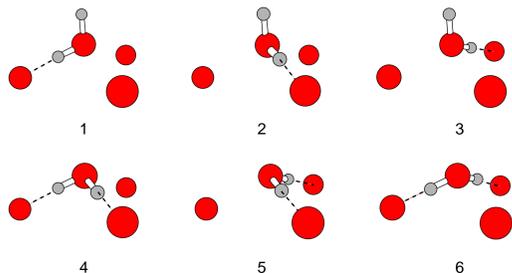


Figure 1: Possible orientations of the water molecules

- each edge of the dodecahedron is a hydrogen bond
- 10 water molecules have one hydrogen atom pointing away from the cluster
- the distribution of these ten water atoms is of primary importance for the total energy of the cluster
- conformations, which can be obtained through manipulation with one of the 120 symmetrie operations are considered to have the same energy
- the conformation with the greatest probability over a wide temperatur range ist best suited for quantum chemical calculations

Processing of the total energies for the different clusters (Boltzmann statistics), obtained with the classical TIP4P interaction potential, resulted in the structure shown in figure 2 as the conformation with the greatest probability (second lowest in energy, but 6360 fold degenerate).

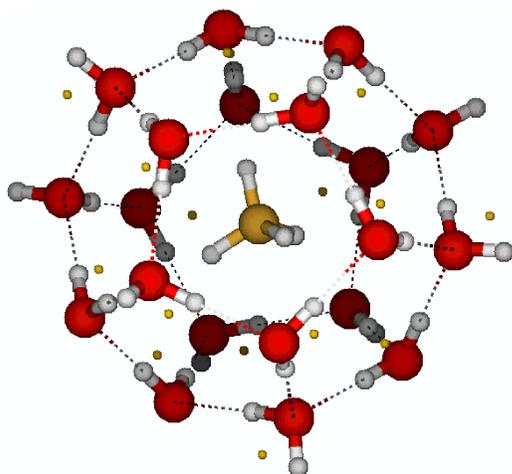


Figure 2: Structure of the water cluster with the greatest probability

## Quantum chemical calculations

The quantum chemical calculations of the  $\text{CH}_4@(\text{H}_2\text{O})_{20}$  cluster are done with Gaussian98. The resulting total energy for different diameters of the cluster, with the B3LYP functional and the 6-31G\*\* basis set on HF-optimized geometry, are shown in figure 3.

Figure 4 shows that the minimum of the interaction energy of the cluster is at smaller values of  $r_{OC}$  (the distance between the carbon of the methane molecule in the centre and the oxygen atom of the water molecule in the dodecahedron) than the minimum for the total energy of the cluster. The methane-water interaction energy curve shows only a shallow minimum at large values for  $r_{OC}$ . The interactions between the methane molecule and the water cage are therefore repulsive for values of  $r_{OC}$  close to that of the minimum of the total energy or the experimental one.

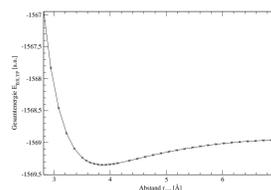


Figure 3: Total cluster energy at different oxygen-carbon distances

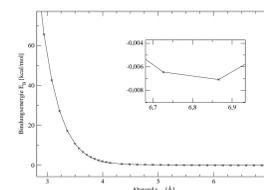


Figure 4: CP-corrected binding energy between methane and the water molecules

## Classical Calculations

A quantum chemical approach which includes more water molecules than the first solvation shell is beyond the scope of modern computational power. For these kind of system exists until today no reasonable alternative to calculations with classical interaction potentials. The necessary interaction potentials are generally derived from quantum chemical calculations for smaller model systems and/or experimental values. This procedure limits the application of these interaction potentials usually to problems similar to that used for the generation of the potential energy functions. Today different potentials for the prediction of thermodynamical and/or structural data for water and methane are used. Table 1 summarises the solvation free energy of methane calculated with the GROMACS program suite for selected combinations of frequently used potential energy functions.

It can be seen that the tested potentials show greater free energy of solvation than the experimental value of -2.0 kcal/mol. It seems therefore useful to create a new interaction potential based on quantum chemical calculations to study the solvation of methane in water.

## Multicenter-Effects

Published quantum chemical calculations [2, 3] and molecular dynamics simulations agree in the bonding character of the methane-water interaction, while our results suggest repulsive forces.

To solve this contradiction we did a full geometry optimisation of the  $\text{CH}_4@(\text{H}_2\text{O})_{20}$  cluster at 6-31G(d)/HF level similar to the calculations published by Sandler et. al. [2]. The HF calculation indicate a weak bond (-2.7 kcal/mol) between the  $\text{CH}_4$  molecule and the  $(\text{H}_2\text{O})_{20}$  cage. A repetition of this calculation with a rigid water cage (as described above) and an  $r_{OC}$ -distance of 4.02 Å (an average value from the optimization) gave a similar result (-2.6 kcal/mol).

The correction of the Basis Set Superposition Error (BSSE) according to Boys and Bernardi resulted in both cases in repulsive interactions (full optimization +2.2 kcal/mol, rigid: +2.3 kcal/mol).

These calculations show clearly, that high-level quantum chemical calculations with the full  $\text{CH}_4@(\text{H}_2\text{O})_{20}$  unit are necessary to understand the chemical nature of the gas hydrates.

Further conclusions of the nature of the  $\text{CH}_4-(\text{H}_2\text{O})_{20}$  bond can be drawn from the analysis of the multicenter energies according to Stillinger et. al. [4] The interaction energies of the complete cluster are dominated by the hydrogen bonds and the pattern of the multicenter contributions resembles therefore that observed in other water clusters [5]. A different behaviour can be observed for the  $\text{CH}_4-(\text{H}_2\text{O})_{20}$  interaction energy. Only the 2-center contributions to the binding energy are attractive while multicenter contributions of higher order are repulsive. A similar behaviour has been observed by us for other  $\text{CH}_4-(\text{H}_2\text{O})_n$  clusters with  $n > 4$  (data not shown here). In summary it seems justified to assume, that the special character of the  $\text{CH}_4-(\text{H}_2\text{O})_{20}$  interaction arises from multicenter effects within the hydrogen bonded network of the  $(\text{H}_2\text{O})_{20}$  cage, which can not be described in a acceptable manner with models basing on any cut through the  $\text{CH}_4@(\text{H}_2\text{O})_{20}$  unit.

## Prospectives

Currently we are working on a computer program, which allows us to calculate the properties of the  $\text{CH}_4@(\text{H}_2\text{O})_{20}$  unit at quantum chemically high levels (including BSSE correction). Our approach resembles that of Stillinger and can be easily parallized, in order to compute cluster even larger than  $\text{CH}_4@(\text{H}_2\text{O})_{20}$  which are necessary for our future model.

Water	Methane	Energy
SPC	OPLS	-2.30
SPC/E	OPLS	-2.55
TIP3P	OPLS	-2.65
TIP4P	OPLS	-7.41
TIP4P	OPLS-AA	-6.33
Exp.		-2.0

Table 1: All energies are in kcal/mol

	complete cluster	$\text{CH}_4-(\text{H}_2\text{O})_{20}$ bond
2 center	-176.8 (83.1 %)	-5.02 (176.7 %)
3 center	-32.6 (15.3 %)	+1.96 (-69.1 %)
4 center	-3.2 (1.5 %)	+0.22 (-7.6 %)
sum	-212.6 (100 %)	-2.84 (100 %)

Table 2: Multicenter energies in kcal/mol in the fully optimized  $\text{CH}_4@(\text{H}_2\text{O})_{20}$  cluster at 6-31G(d)/HF level