ADSORPTION OF WATER AND ACETONITRILE ONTO OCTADECYLSILANE

1. <u>INTRODUCTION</u>

Chromatography is a biophysical technique used to separate mixtures in analytical chemistry (1). The underlying principles of separation are dependent on the type of molecular interactions and the actual size of the components of the mixture. There are many types of chromatography in use in the laboratory but one of the most versatile is High performance liquid chromatography. In this chromatography there is a stationary phase and a mobile phase. The stationary phase generally consists of modified silica gel whose surface has organic chains i.e. octadecylsilane while the mobile phase is usually a mixture of solvents of water and methanol or acetonitrile. The mixture to be separated is introduced into a column which has a lining of the stationary phase and is moved through the column by the mobile phase. As the mixture of analytes moves through the column the components are separated from each other depending on their interaction with the stationary phase. Those that interact most come out the column last and those that interact the least come out the column first. There are many more details to be considered before attempting to separate a mixture but those are not of interest in this initial study.

In my previous work, we deployed molecular dynamics simulation technics to try and deduce the level and types of interactions that occur between an analyte and the mobile phase at different compositions of the mobile phase. This study allowed us to explore the possible applications of these simulations in replicating the expected experimental results. In this work the same approach will be used but I will be studying the interactions of the mobile phase with the stationary phase to try and show the applicability of the Density Functional Theory and its counterparts to such systems.
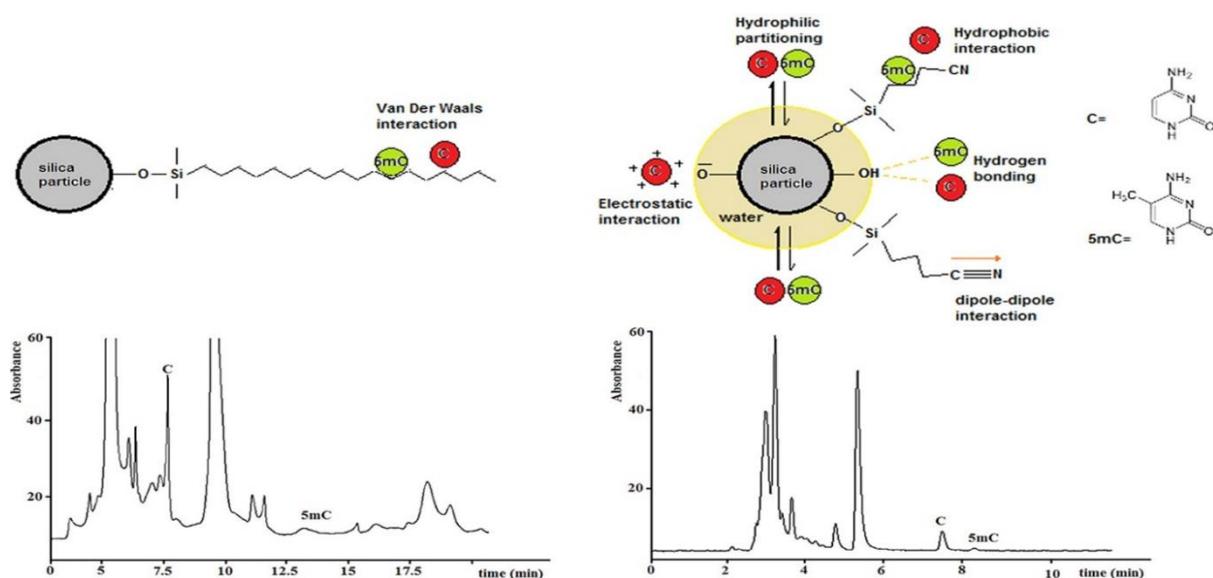

Fig1. Interaction between an analyte (5mC, C) and the stationary phase (silica particle).

2. ADSORPTION

Adsorption is the adhesion of a substance onto the surface of a solid or liquid without the formation of an actual chemical bond. There are two types of adsorption, physical and chemical adsorption. In physical adsorption the dominant forces are van de Waals forces and the adsorption can easily be overcome by an increase in temperature. In chemical adsorption the adhesion forces are as strong as a chemical bond and the adsorption cannot be easily reversed. In Fig.1 above, on the top left corner is physical adsorption between analytes and the stationary phase. This type of adsorption can be studied at a lower accuracy using molecular dynamics techniques. In this paper we will study the adsorption of the mobile phase onto the stationary phase using DFT for an expected higher accuracy.

Our stationary phase is octadecylsilane and our mobile phases are water and acetonitrile. Since the mobile phases are polar and the stationary phase is non polar we do not expect an adsorption to actually take place but this will be confirmed after the calculations are performed. The accuracy of the results will determine if DFT is a suitable method for simulating adsorption of organic molecules and systems of the same nature.

3. METHOD

The system to be studied consisted of three molecules, water, acetonitrile and octadecylsilane. The crystal structures for these molecules were made in house using Avogadro software (3). Parameters for the crystal of octadecylsilane were approximated from the crystal structure of n-octadecane (4). For water and acetonitrile arbitrary parameters were used.

The simulated surface consisted of two octadecylsilane molecules with only one layer. Using one layer is sufficient for these calculations because the organic surface is only repeating its pattern in the x and y coordinates and not in the z direction unlike metal surfaces.

All the calculations were done using the PWSCF program found in quantum espresso (2) using computational resources provided by TRUBA (7). Firstly, Determination of the optimum parameters (ecutoff, kpoints...etc.) for the molecules in our system was achieved by running scf calculations on the bulk of the molecule at different cut-off energies. The obtained results were then used to choose reasonable input parameters to be included in the relaxation calculations.

For octadecylsilane, from Fig.2 the minimum energy of the bulk decreased with the increase in energy cut-off but a lower cut-off energy of 40Ry was selected for the study because the relaxation of the octadecylsilane surface at higher cut-off energies was not successful due to the computational time limits. Water and acetonitrile displayed a similar minimum energy vs energy cut-off relation but did not face the same obstacle. Thus, a cut-off energy of 150Ry was chosen after which the change in the minimum energy of the bulk is negligible as shown in Fig.3 and Fig.4.
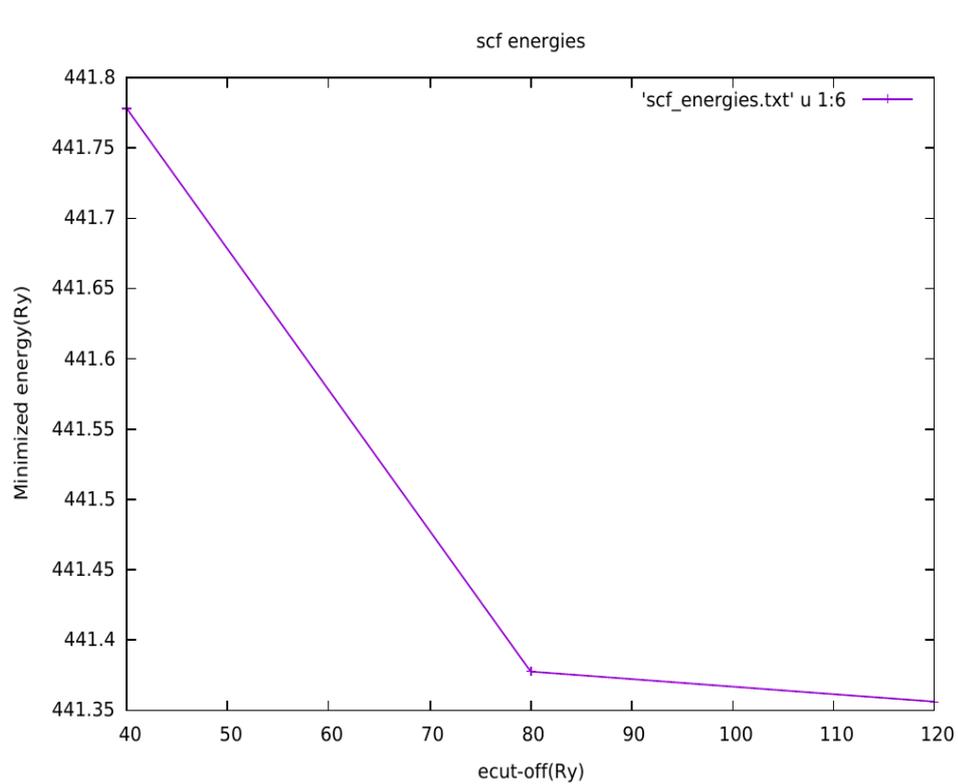
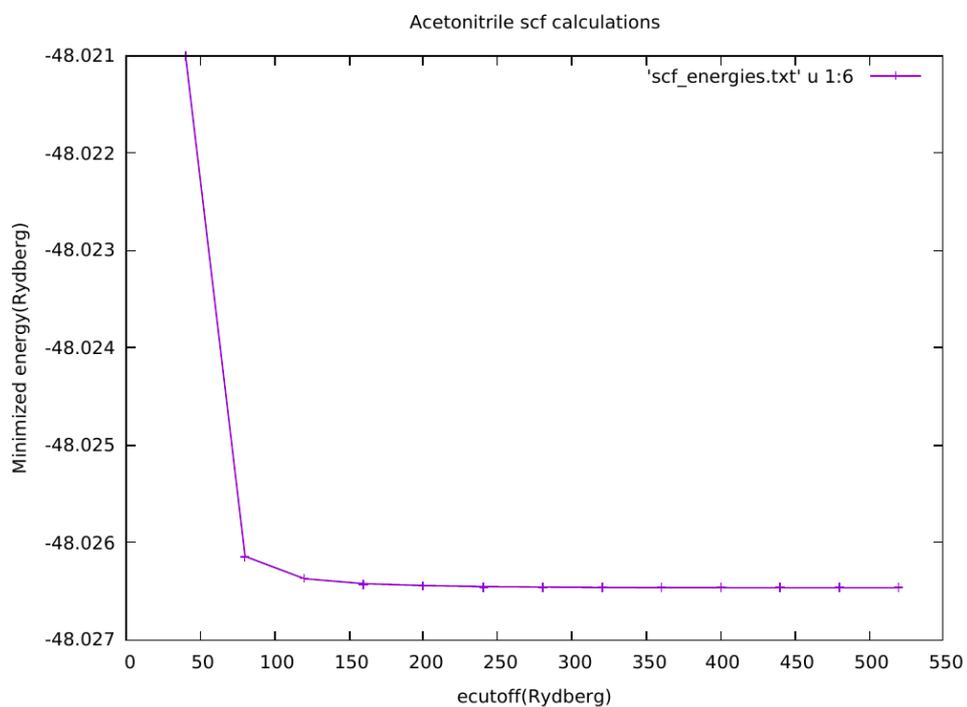Fig2. Octadecylsilane graph of Minimized energy vs energy cut-off.

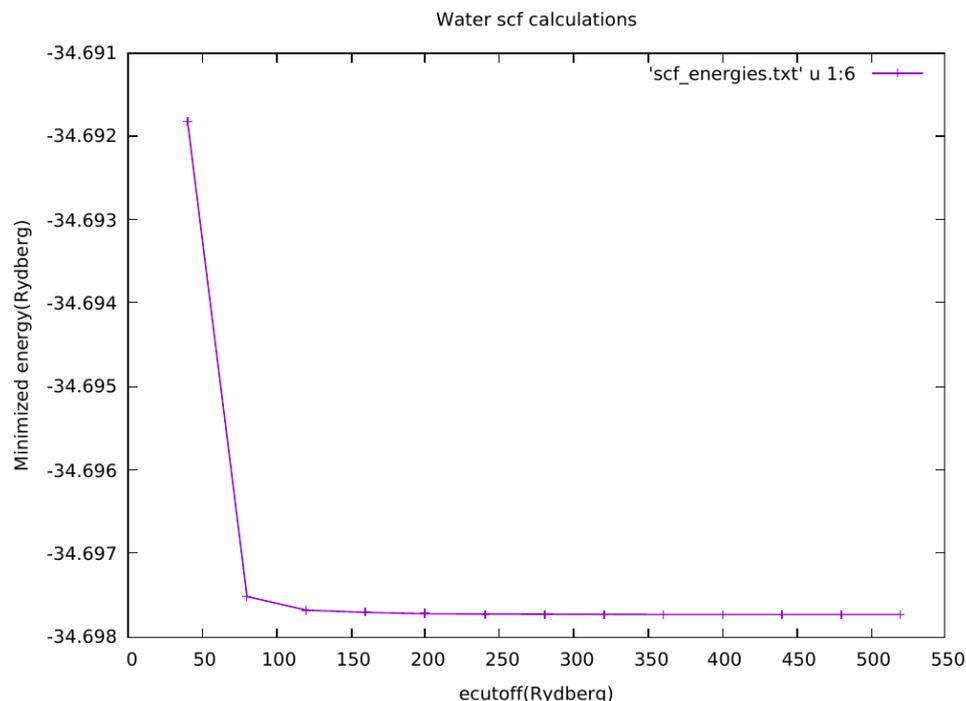Fig3.Acetonitrile graph of Minimized energy vs energy cut-off.

Fig4.Water graph of Minimized energy vs energy cut-off.

The generic input format that was implemented for all the calculations of the bulk and relaxation is as shown below:

&control

&system

&electrons

&ions

ATOMIC_SPECIES

ATOMIC_POSITIONS

CELL_PARAMETERS

K_POINTS

Under each namelist and card different input parameters were selected according to the needs of the calculation. The only constant input parameters for all calculations were under the system namelist where by occupations =smearing, smearing = "mv" and degauss = 0.02. No advanced adjustments were made in the input and most of the options were left to default. The pseudopotentials used for all calculations were ultra-soft pseudopotentials (8).

For the calculations of adsorption, the parameters adopted were those from octadecylsilane relaxation since it determines the optimum conditions for successful calculations as it holds the highest number of atoms in the system.

4. RESULTS AND DISCUSSION

The molecules of water and acetonitrile were placed at arbitrary distances from octadecylsilane assumed to be optimum for adsorption. This was performed in Avogadro software and the geometries of water and acetonitrile were optimized after the allocation around the octadecylsilane surface. To clearly sample the total energy of adsorption two sites of adsorption were chosen for water and acetonitrile, vertically on top of the octadecylsilane and in between two octadecylsilane chains as shown in figures 5 to 8.

The obtained outputs from the relaxation of the water+octadecylsilane setup of adsorption showed that the hydrophobicity of octadecylsilane did not allow the positioning of water molecules anywhere close to it. As shown in Fig.5 and Fig.6 the water molecule is readily being repelled by the octadecylsilane chains when placed in both sites of adsorption. This was to be expected since it is known that polar molecules prefer the least possible interaction with non-polar molecules.

Since our setup was not a conventional one for the study of surfaces, the calculation of surface energies and of adsorption were done differently. To determine the adsorption of our molecules we calculated the relaxation energies of our systems when combined and when separated. Subtracting the sum of the separate relaxation energies from the combined relaxation energy will give us the value of the adsorption energy. If the value is negative, then the adsorption is favourable and if positive unfavourable. Even though the outputs display hydrophobicity the calculated energies are negative except for one setup as shown in Table.1.

Adsorption sites	Adsorption energy (Ryd)	Adsorption energy (kcal)
oct+wat1	0.15464933	48.52195543
oct+wat2	-0.06009973	-18.85657326
oct+wat2_gpu	-0.0662759029	-20.79437659
oct+aceto1	-0.4422598	-138.7610946
oct+aceto2	-0.49405821	-155.0130896
oct+aceto3	-0.51558558	-161.7674033

Table1. Adsorption energies of the mobile phase onto the stationary phase. ('wat' stands for water 'aceto' stands for acetonitrile and 'oct' for octadecylsilane)

This was initially thought to most likely be a consequence of the limited number of steps that were allowed for the relaxation calculations. In the inputs it was set at default which is only 50 steps. This number of steps could be feasible for normal calculation but not for our setup. An increase in the number of steps will help the system come closer to convergence but it will bring with it longer computational times and the need for higher processing power. We put this assumption to a test by running the adsorption of water at the second site using a gpu with 40 cores, nstep=500 and for 9 hours. The convergence was achieved after 110 scf cycles. The results of this run are presented in Table.1 as "oct+wat2_gpu". As it can be seen the adsorption energy is still negative and at a much lower energy meaning that the orientation of the molecules in the last step are favourable. Checking the orientation from the initial and final steps in Fig.9 the water has been pushed to the furthest distance from both octadecylsilane chains thus hydrophobicity has been achieved.

Acetonitrile is also a polar molecule so the results from the output showed the same behaviour where polar molecules look to be repelled by nonpolar molecules as shown in Fig.7 and Fig.8. The different sites and positioning of the molecule both gave the same result.

It is not easy to discern the differences in positions of the mobile phase from the stationary phase because the number of cycles were not enough to give a dramatic difference in positions between the first and last step. But by looking at the movies attached in this document with the xcrysden (5)

program it becomes clearer. After installation of xcrysden the movies can be watched by running the following command on the terminal:

xcrysden --pwo filename

Outputfiles: oct+wat1 oct+wat2 oct+wat2_gpu oct+aceto2 oct+aceto3
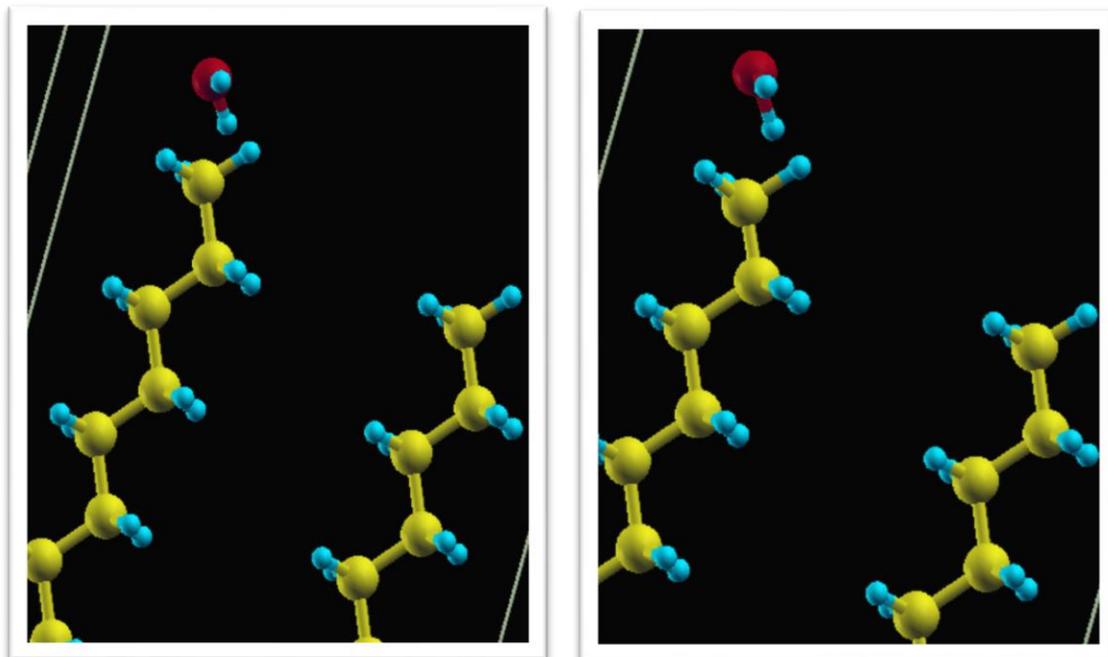

Fig5. Adsorption of water at the first adsorption site the initial and final steps displayed from left to right.
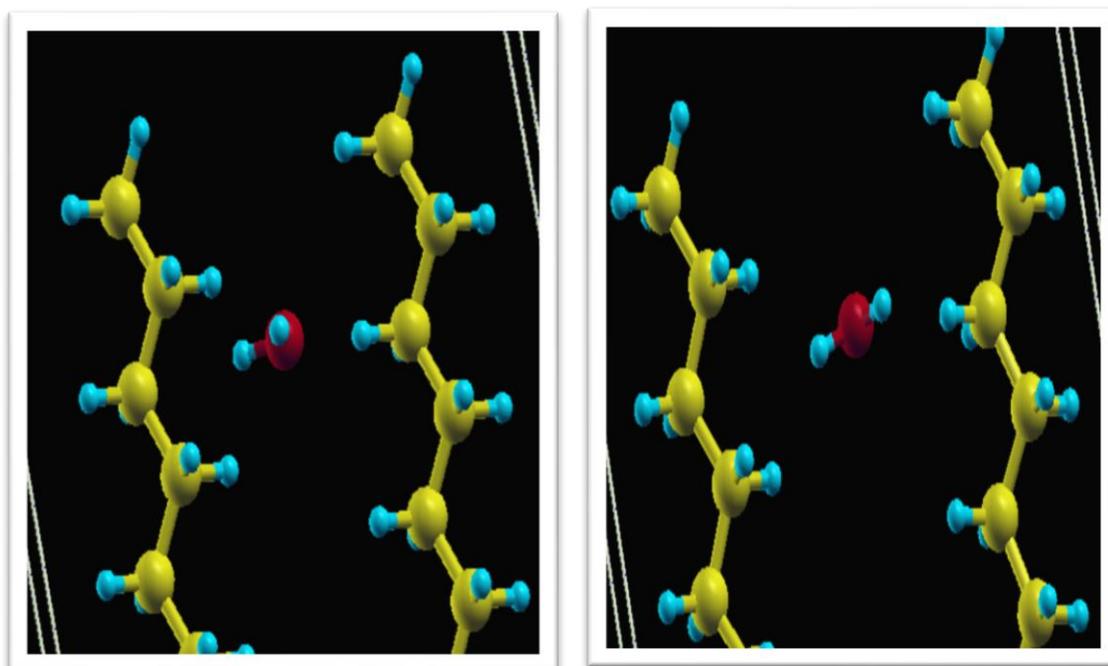

Fig6. Adsorption of water at the second adsorption site the initial and final steps displayed from left to right.
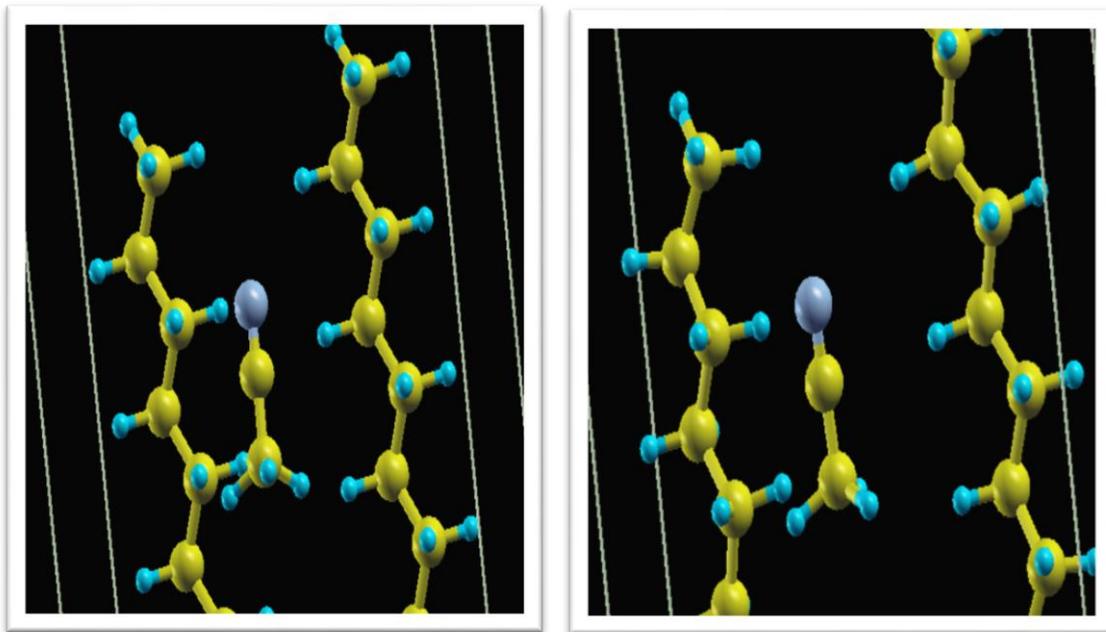
Fig7. Adsorption of acetonitrile at the second adsorption site the initial and final steps displayed from left to right.
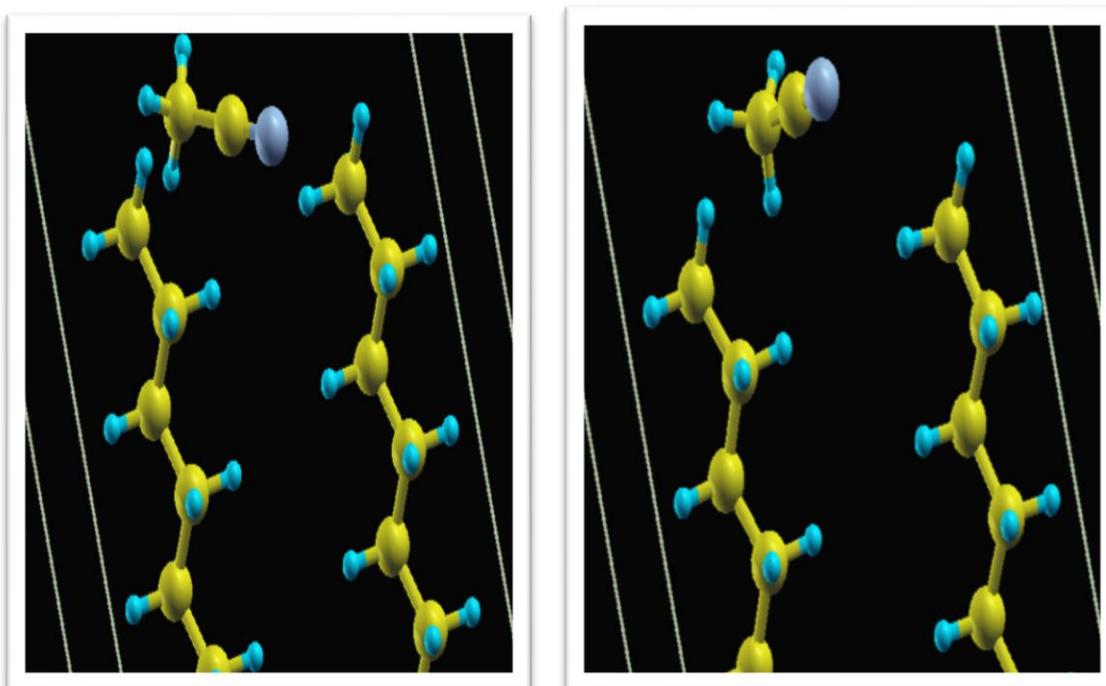

Fig8. Adsorption of acetonitrile at the first adsorption site the initial and final steps displayed from left to right.
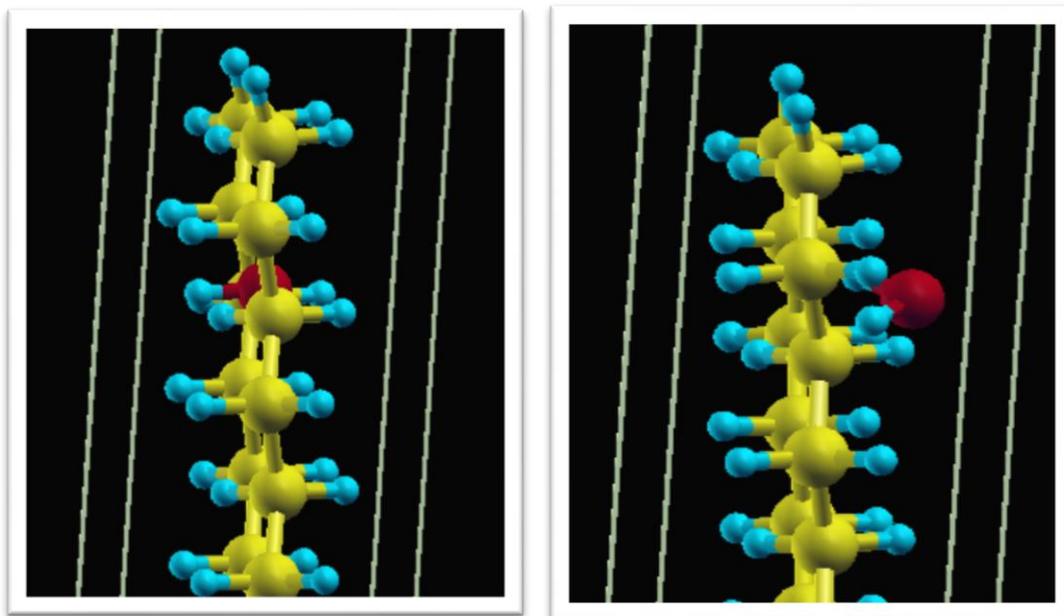
Fig9. A lateral view of the converged water adsorption on the second site. The initial and final step are displayed from left to right respectively.

5. <u>CONCLUSION</u>

To fully utilize the power of DFT in analysing any type of molecular interaction in chemistry, contrast to material sciences one needs to prepare the smallest system possible and allocate the highest amount of time and resources available at their disposal. In order to get reliable results onto which analysis can be performed, a thorough optimization of the system has to be made since there isn't much information on the exact parameters to be used for most organic compounds in published literature. The optimization procedure is time consuming and the resulting setup may not be very suitable for your given system and that will definitely affect your results. For example, the adsorption of water on the first site made only 2 scf cycles because the second cycle had done 100 iterations without reaching convergence. This may have been due to the distance set between water and octadecylsilane or totally something different. An educated guess can be made before running the calculations but generally it is hard to spot the problem until the calculations have been performed which leads to a time-consuming endeavour.

It would have been of great interest to investigate more adsorption sites and the underlying surface of the stationary phase which is a silicon dioxide crystal modified with hydroxides bonded to silicon on its surface. These columns with hydroxides are known as uncapped columns and those that have replaced the hydroxide with more nonpolar compounds are referred to as capped columns. The use of one or the other has an effect on the resolution of the output in chromatography.

Other methods that could be cheaper and give more or less equivalent results for the adsorption energies of the mobile phase and even its analytes simultaneously are Molecular Mechanics and DFT-MD. These methods are promising because the sufficient solutions needed to analyse the van

de Waals forces in play during the interaction between organic compounds can be generated to simulate the interaction within a given duration in time which is of more interest to chemists.

There isn't much effort that is being made to understand exactly what happens during chromatography because the existing standards are working just fine. A lot of the physical phenomena affecting chromatography at a macroscopic level have been studied and are readily applied in practice. I am of a strong opinion that the ability of these methods will hit a wall soon enough and we will have to go back to events happening in the molecular scale and ask the same questions on why the separation works.

With this work, although very little was done, we have managed to show that DFT and similar methods to it can be used to study the entire chromatographic separation process given that sufficient resources and time is allocated towards the research. Co-operation between experimental analytical chemists and computational chemists could bring a completely new understanding to chromatography and open doors to development of new chromatographic techniques in the future.

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8. [PSEUDO] We used the pseudopotentials C.pbe-n-rrkjus_psl.1.0.0.UPF, N.pbe-n-rrkjus_psl.1.0.0.UPF, O.pbe-n-rrkjus_psl.1.0.0.UPF, Si.pbe-nl-rrkjus_psl.1.0.0.UPF and H.pbe-rrkjus_psl.1.0.0.UPF from the Quantum ESPRESSO pseudopotential data base: http://www.quantum-espresso.org/pseudopotentials.

LINKS TO SHARED FILES

1. https://drive.google.com/file/d/1ClAr8dnWVoBG3TILms1fZ9dO-DK51C10/view?usp=sharing

2.https://drive.google.com/file/d/1ppflp-b18SPPevh1towZ1yZGQINpSV19/view?usp=sharing

3.https://drive.google.com/file/d/1GxZJ7G4rU552pBTRlCUFcQUGrguFehic/view?usp=sharing

4.https://drive.google.com/file/d/1pQUlgISLTTluG2bnQfC15YRQONYLzvJx/view?usp=sharing

5.https://drive.google.com/file/d/1ymWWJHV3k_slSfd3hVTsqPWvoFk0Z4Cu/view?usp=sharing