

Intercalation of molecules into graphite-nitrate

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Abstract

Intercalation is enlarging the spacing between graphene layers as creating a bigger volume where the gas molecules such as hydrogen can be stored. In this project we focus on the intercalation of graphite-nitrate with stable/robust molecules, which can act as pillars in between the graphene layers. The molecules used here were C₆₀, ethylene glycol, cyclohexane and adamantane, however, only for C₆₀ and adamantane the intercalation was successful. The starting material was the β -crystalline form of graphite-nitrate, with a spacing along the c-axis of 6.61 Å. For C₆₀ the spacing increased to 9.1±0.1 Å and for adamantane we found spacings of 20.05±0.03 Å and 10.39±0.04 Å. Further research has to be done concerning the intercalation of adamantane in graphite-nitrate to determine in which way these molecules bind to graphite-nitrate.

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1. INTRODUCTION

Nowadays a lot of research is devoted to new types of fuels since the amount of fossil fuels, which is readily exploitable, will be depleted in the near future. This fact, in addition to the assault of the environment, requires searching for a cleaner and sustainable solution such as hydrogen power.

Hydrogen can be stored as a liquid or a gas and its storage has to be efficient. The storage requirements¹ for gaseous storage established by the United States' Department of Energy are that the gravimetric density should be 6 weight-% and the volumetric capacity 45 g of H₂/L. To meet these requirements an appropriate nanoporous/mesoporous material with high surface area has to be developed, capable of absorbing large amounts of hydrogen. Initially metal alloys were proposed for storage but they are expensive and extremely heavy for commercial use. Another option is a light and robust nanoporous material, which can store hydrogen by physisorption. In physisorption the electronic states of absorbant and storage material do not hybridize since only weak bonds occur due to the induced dipole moment.¹

One of the best candidates in this direction is graphite, where the hydrogen molecules can be stored between the graphene layers.² For this to occur, the graphite has to be intercalated, meaning that the spacing between graphene layers has to be enlarged as to create a bigger volume where the gas molecules can be stored. In this project we focus on the intercalation of graphite with stable/robust molecules, which can act as pillars in between the graphene layers. To achieve this, it is essential to utilize a co-intercalant capable of opening the space between the graphene layers in the starting graphite and hence facilitate further intercalation. The co-intercalant employed in our case was nitric acid. The graphite intercalated with nitric acid is therefore our starting material. Its characterization shall be detailed in chapter 2 of this report.

It is possible to co-intercalate other molecules or atoms such as alkali metals.³ After co-intercalation the compound becomes superconducting at a transition temperature (T_c) lower than 33 K. Because the alkalis are extremely reactive, these materials are not stable in air and therefore difficult to handle, so we do not consider them useful starting compounds for our purposes.

The method we used for intercalation of graphite-nitrate depended on the type of molecule we wanted to insert. Essentially our aim was to explore if intercalation occurred for our molecules of choice. For this we determined the spacing between the layers. We also wanted to find out whether the molecule was chemically bound to the starting material or just physisorbed. This information can be deduced from X-ray photoelectron spectroscopy measurements of our samples.

This report is organized as follows: In Chapter 2 we describe the materials and the characterization techniques we employed, in Chapter 3 the experimental protocol for intercalation is detailed, in Chapter 4 we report the results of this study and finally the last chapter contains the discussion, conclusion and recommendations.

2. MATERIALS AND CHARACTERIZATION TECHNIQUES

2.1 Graphite-nitrate

As we mentioned above the initial material for the further intercalation of graphite is graphite-nitrate. The nitric acid groups are arranged between the alternating graphene layers and bound to them by weak Van Der Waals forces. According to the orientation two arrangements can occur, the so-called α -crystalline⁴ and β -crystalline forms as shown in figure 1. This figure illustrates the repeating structure which makes up the crystal in each case. These crystalline forms could be demonstrated by measuring the distance between the graphene planes by X-ray diffraction. The α -crystalline form is metastable and transforms at room temperature into the more energetically favourable β -crystalline form.

The difference between these two forms is the coordination of the nitrate-group; which can be perpendicular or parallel to the graphite layers. As a consequence of this different orientation the distance between the graphite layers changes. As seen in figure 1,⁵ we can describe the identity period with the equation $I_n = d_i + 3.35(n - 1)$. Here 3.35 \AA is the lattice constant of a pure graphite layer along the c-axis; d_i is the lattice constant when all the planes are intercalated meaning that a stage one compound is formed; n indicates the stage, which is defined by how many layers there are interposed between the intercalated molecules. In figure 1 this number is two.⁵

For the α -crystalline and β -crystalline forms of graphite-nitrate d_i is found to be 7.80 \AA and 6.55 \AA , respectively.⁶ The stoichiometry of these compounds is $C_{24n}^+ NO_3^- 5HNO_3$ and $C_{24n}^+ NO_3^- 2HNO_3$.⁴

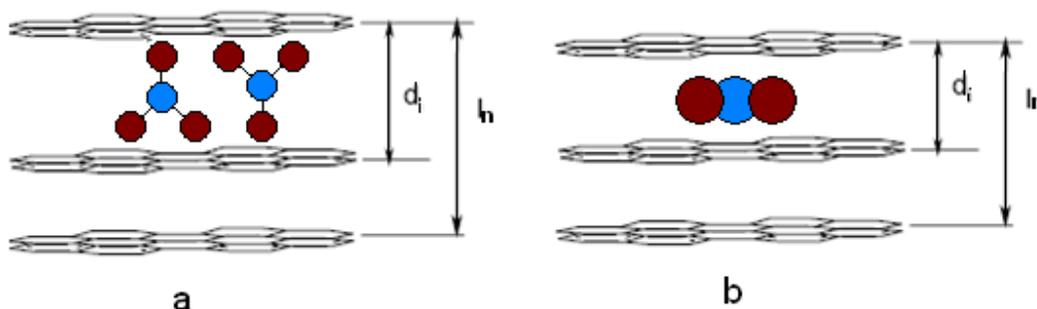


Figure 1: Identity period of by 2nd stage a) α -graphite-nitrate and b) β -graphite-nitrate

Graphite reacts spontaneously with nitric acid and gives a stage one graphite intercalation compound.⁷ However, this compound is not stable and reverts spontaneously to a stage two compound when exposed to air. This compound is also called residual graphite-nitrate.⁸ Graphite-nitrate can be retransformed into graphite (de-intercalation) by heating to a temperature more than $75 \text{ }^\circ\text{C}$.⁷

2.2 Molecules tested for intercalation

We tested both polar and non-polar molecules as intercalants. For each type the interaction with the nitrate-groups is expected to be different and therefore also the intercalation yield more or less efficient.

Another way of classification is to look at what compounds, donor or acceptor,² are formed. A donor donates electrons to the other material and an acceptor accepts them. Normally donor compounds are formed due to intercalation of alkali and acceptor due to intercalation of acids. These donor compounds are known to be less stable, because they want to get rid of the excess of electrons. Depending on the kind of intercalant used, there will be a charge separation between the molecule and graphite layer, so a donor or an acceptor compound is formed.

In this experiment four molecules were tried for intercalation into the graphite-nitrate, C₆₀, adamantane, ethylene glycol and cyclohexane. Intercalation of C₆₀ in graphite has been done before, so a bit more information about some properties is available.³

2.2.1 C₆₀

C₆₀ or buckminsterfullerene is made up by 60 carbon atoms and has the shape of a football with twenty hexagons and twelve pentagons of carbon, as shown in figure 2. Spheres are known to be the most stable configuration in nature, this holds true also for C₆₀. Compared to other carbon molecules C₆₀ is inert, however, when exposed to light and oxygen at the same time it readily decomposes. C₆₀ is known as the only carbon allotrope to be soluble.³ Soot contains a lot of C₆₀ molecules, but due to the decomposition we rarely see them, so normally they are prepared by producing an arc-discharge between graphite rods⁹ or by a twelve step synthesis.¹⁰ Because of the hollow structure of C₆₀ atoms can be inserted inside the cage.¹¹

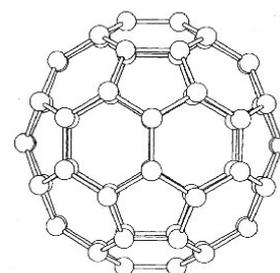


Figure 2: C₆₀

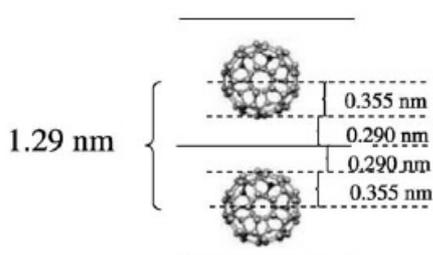


Figure 3: Calculation of the C₆₀ center-to-center distance in the intercalated graphite.

As illustrated in figure 3, the radius of C₆₀ is 3.55 Å and the Van der Waals diameter is 2.90 Å.^{Error!}

Bookmark not defined. This diameter describes the distance till the next atom; which derives from the equilibrium between repulsion and attraction. From the research that has been done in the intercalation of C₆₀ in graphite,³ we already know that the average distance between two adjacent layers is 12.9 Å (see figure 3). This fits perfectly with two times the sum of the radius and the Van der Waals diameter. The nearest-neighbour distance of the centers is $a = 9.824 \text{ \AA}$.

It is expected that this compound is chemically rather stable in the air,¹² because graphite is stable and C₆₀ is partially protected by the graphene sheets. The previous study also

found that the bottom and top of each C_{60} -cluster are parallel to the graphite hexagons.³ In graphite electrical conduction is much larger within the planes than perpendicular to them. After intercalation a small charge transfer can occur from the graphite to the C_{60} layer, as well as redistribution of electrons within the graphene layer. For this it is important to know that fullerene is an electron acceptor.

2.2.2 Ethylene glycol

Ethylene glycol ($C_2H_6O_2$) consists of carbon atoms both attached to a hydroxy-group as seen in figure 4. At room temperature this polar molecule condenses into a colourless and odourless liquid, with a molecular weight of 62.07 g/mol. This liquid is normally used as an antifreeze agent; it has good heat transfer capabilities and a low conductivity. Since ethylene glycol is not expensive, it is abundantly used as solvent.¹³ The boiling point of ethylene glycol is 470.5 K.

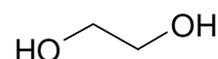


Figure 4: Ethylene glycol

The size of one ethylene glycol molecule can be determined because the distances and bond angles between the atoms are known.¹⁴ With this determination it is found that the length of the molecule is approximately 3.14 Å.

2.2.3 Cyclohexane

Cyclohexane (C_6H_{12}) consists of a ring of six carbon atoms; the simplest conformation is the planar one, as seen in figure 5a, where the angles must be 120° . Since this geometry puts some strain on the bonds and causes some overlap between the hydrogen orbitals the planar cyclohexane can not be the groundstate configuration. So the molecule will transform to the chair conformation, as seen in figure 5b, or to the boat conformation; these molecules are strain-free.¹⁴ In the planar configuration the size of this molecule is about 3.08 Å, this is the distance between the two farthest-away carbon atoms.

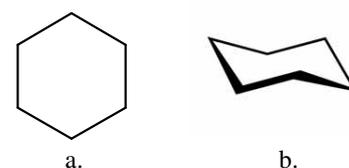


Figure 5: Cyclohexane conformations
a) planar and b) chair

At room temperature cyclohexane is a non-polar colourless liquid with a molecular weight of 84.16 g/mol; its boiling point is 353.85 K, which is almost the same as for benzene.

2.2.4 Adamantane

Adamantane ($C_{10}H_{16}$) is a molecule that can be isolated from petroleum or synthesized in the laboratory. It consists in three connected cyclohexane rings as seen in figure 6 and weighs 136.234 g/mol. It is unsolvable in water, but solvable in non-polar organic solvents.

The C-C bond length is 1.54 Å and all the angles between the carbon atoms are 109.5° . The strong diamond-like carbon-carbon bonds hold this molecule together. The much weaker intermolecular bonds are used to form a crystal.¹⁵ Adamantane crystallizes in a face-centred cubic lattice at room temperature with $a=9.246$ Å.¹⁶ When cooling the molecule below 208.62 K, the lattice changes to a

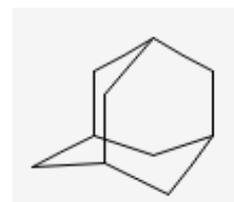


Figure 6: Adamantane

body-centred tetragonal lattice with $a = 6.641 \text{ \AA}$ and $c = 8.875 \text{ \AA}$. As a consequence the density also changes from 1.18 g/cm^3 to 1.08 g/cm^3 .¹⁵

Another remarkable property of adamantane is its incredibly high melting temperature of 543 K which is the highest known for hydrocarbons.¹⁶

2.3 X-ray Photoelectron Spectroscopy (XPS)

XPS is the most widely used surface analytical technique for quantifying the composition of a surface. The surface of a solid is irradiated with monochromatic X-rays and the energy of the photon is transferred to core level electrons, which can leave the solid with a certain kinetic energy, as seen in figure 7a.¹⁷ The kinetic energy, KE, of these emitted electrons is measured and the binding energy, BE, is deduced from $KE = h\nu - BE - \phi_s$.

Here $h\nu$ is the energy of the photon, and ϕ_s is the work function of the spectrometer. Note that BE is defined as the difference between the initial and final state. Each element gives rise to a unique spectrum with one or more peaks at specific binding energies.

Besides the peaks of every element, some extra peaks can occur in the XPS spectrum from Auger processes as seen in figure 7b. This is a decay of the core hole, which, for light elements, takes place within approximately 10^{-15} seconds after emission of an electron. In this process an electron from a shallower orbital fills the core hole and the free coming energy is transferred to another electron which can leave the solid and be detected.¹⁸

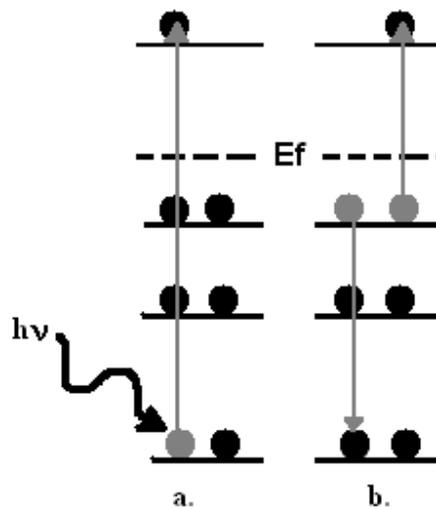


Figure 7: processes contributing in the XPS;
a. excitation of the core electrons
b. hole de-excitation via the Auger process

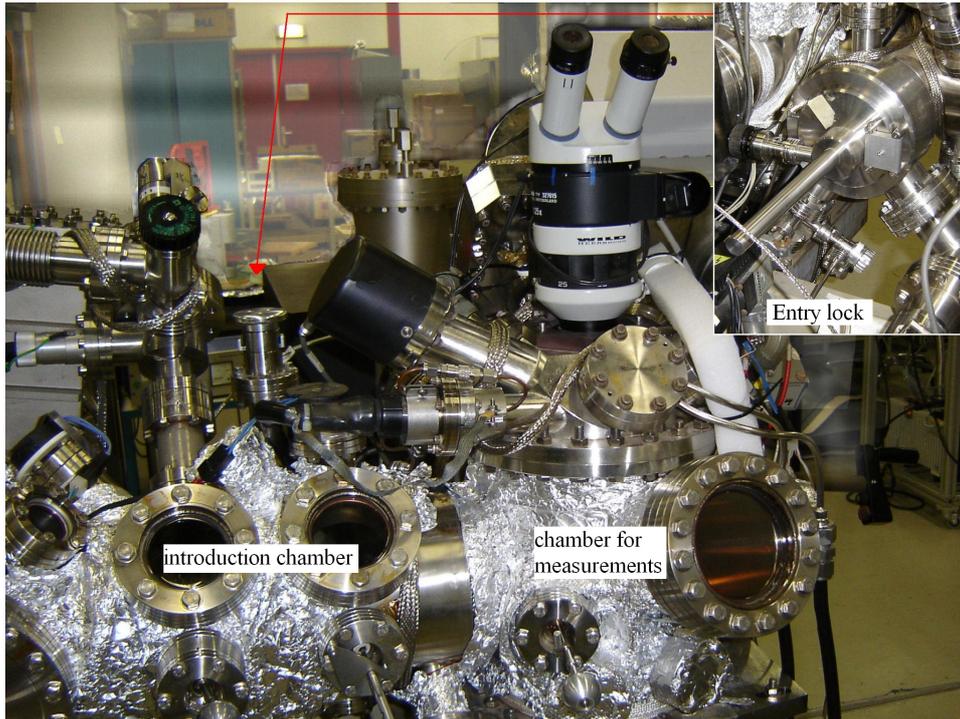


Figure 8: the XPS apparatus

Figure 8 presents a photo of the XPS apparatus, where measurements are done in ultra high vacuum (10^{-10} mbar). In this vacuum the ejected electrons have a long mean free path compared to the internal dimensions of the spectrometer. The vacuum also assures a low partial pressure of reactive residual gasses as to not alter the surface composition by adsorption during the measurement.¹⁹ The procedure of inserting a sample for measurement must be followed tightly. In the beginning the sample is placed in the entry lock, where high vacuum is created. Then the sample is transported to the preparation chamber at ultrahigh vacuum. From there it is transported to the last chamber for the measurements. Before the measurement can be started, the sample must be put into the focus of the analyzer.

After this positioning an overview scan is collected;¹⁷ as seen in figure 9; at specific binding energies, depending on the elements present, peaks are found. One or more of these peaks of the overview scan are from the substrate on which the sample is deposited on. For conducting samples these peaks can be used as reference for the energy scale. Other peaks that could appear in this scan can be some unwanted contaminations. Based on the information of the first scan, some detailed scan of the core level regions of the elements of interest are performed for precise determination. It is important to keep in mind that some compounds can be subject to radiation damage; therefore the stability of the sample has to be verified.

In figure 9 there is an overview scan of the graphite-nitrate and the detailed of the C1s-core level region. The C1s spectrum can be fitted with several components, because the binding energy changes with chemical environment. So this can be used to quantify the

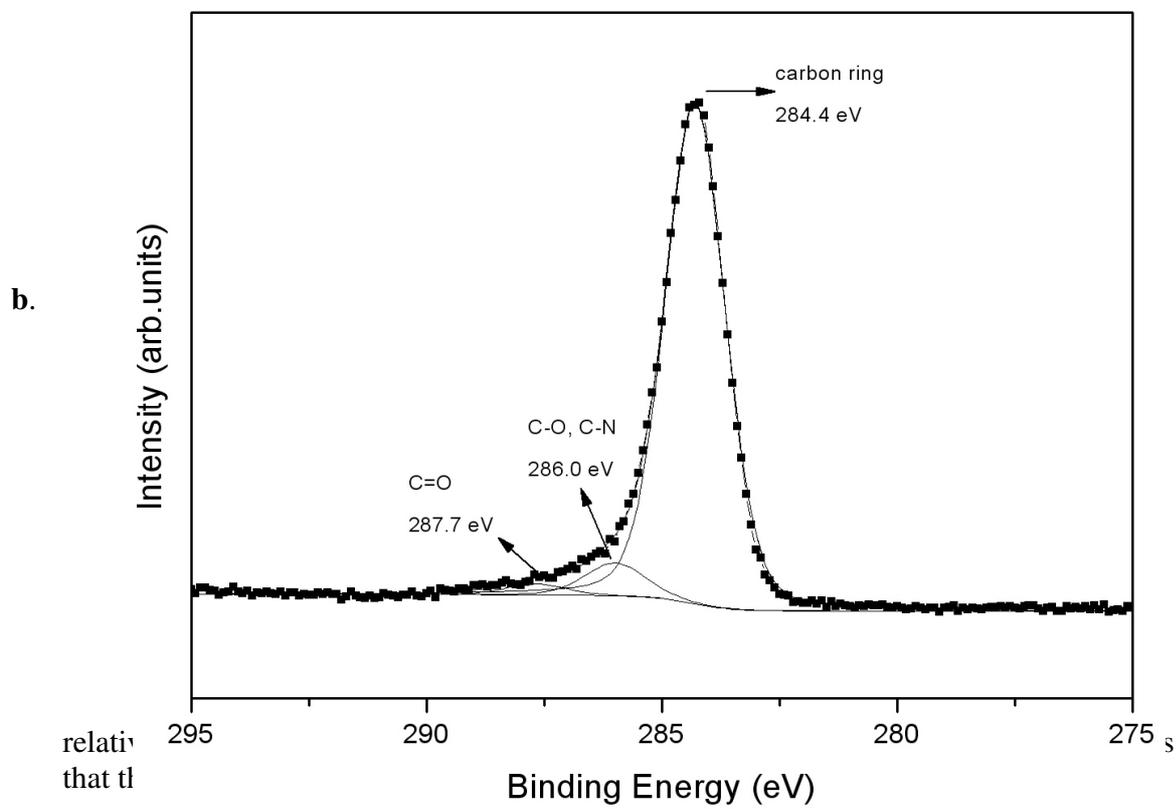
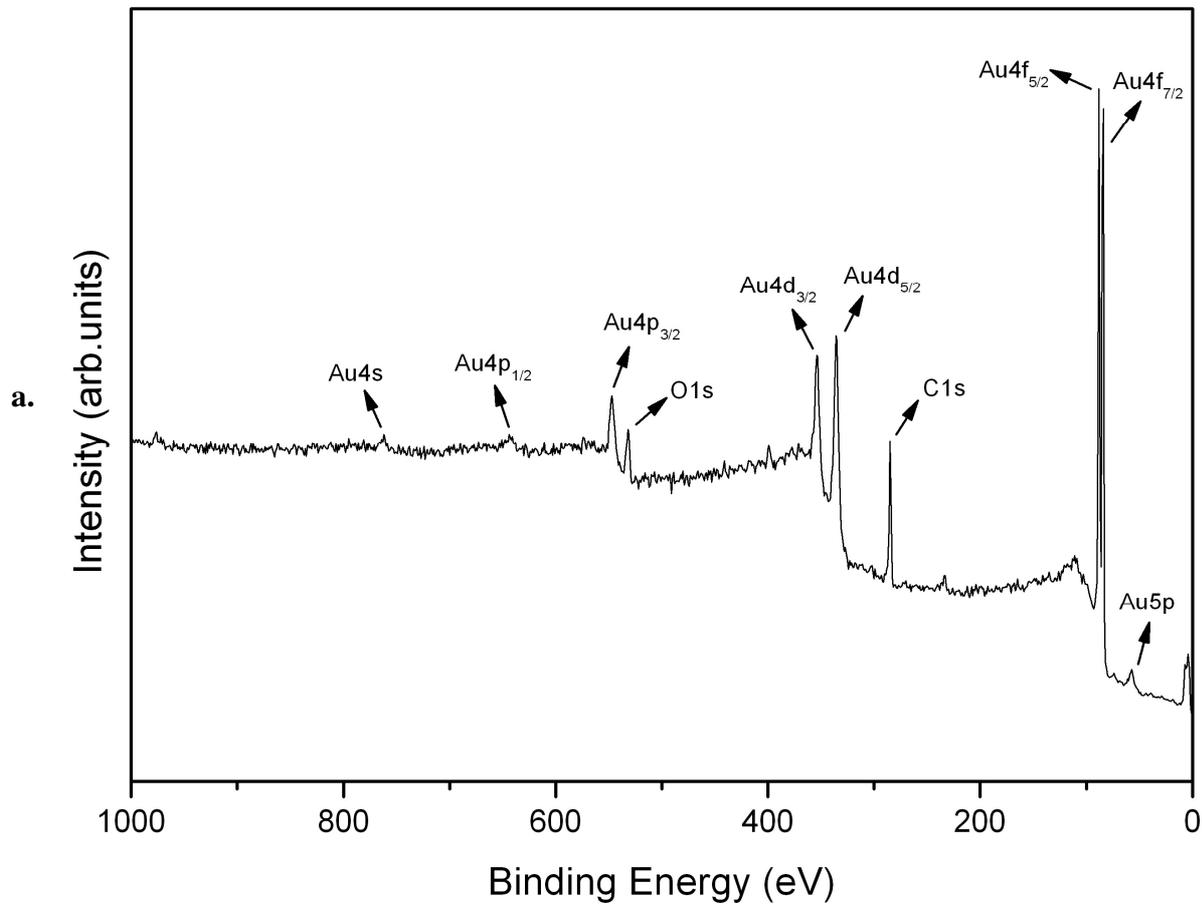


Figure 9: a) Overview scan of graphite-nitrate and b) the detailed peak of C1s-core level region.

The shape (and width) of the peak is determined by various factors. First there is some Lorentzian lifetime broadening because the photo ionization process takes about 10^{-17} seconds and the core hole level decays in 10^{-15} seconds; this gives an indetermination in energy by the Heisenberg uncertainty principle.

The peaks also have a Gaussian broadening due to the vibrations in the solid, because the temperature is not absolutely zero. The peak shape can be influenced by extrinsic losses, in the bulk or at the surface.

Finally, in addition to the final state, where only the photoelectron leaves the solid, there are other final states possible, where more electrons are excited. The conservation of energy implies that these final states correspond to a photoelectron leaving with a smaller kinetic energy. Therefore these final states appear at higher binding energy in the spectrum and are called “shake up” features. Of course there will also be some broadening of the peaks caused by the instrumental resolution¹⁸ and this is dominant in our case where the resolution amounts to 1.2.

Since in practice, XPS may not distinguish between the various types of atoms of the same element present in a molecule, the fitting procedure consists in reconstructing the XPS spectrum with a minimum number of peaks consistent with the raw data, the experimental resolution and the molecular structure, in which atoms of the same element under very similar chemical environments, i.e. very close in binding energy, are considered equivalent and represented by one peak. When more than one component was needed to reproduce the raw data, the error in peak position was ± 0.1 eV. All the measurements were accomplished on freshly prepared samples in order to guarantee the reproducibility of the results.

The intensity of the peaks depends on a number of factors and can be summarized in one formula¹⁷: $I_i = n_i \Phi \sigma_i \theta \lambda_i y_i A T_i$, where

n is the number of atoms per cm^3 ,

Φ the photon flux (in s/cm^2),

σ the photo-electric cross-section,

θ the angular efficiency factor for the instrumental arrangement,

λ the mean free path,

y the efficiency for formation of photoelectrons of normal photoelectron energy,

A the area of the sample and

T the detection efficiency.

This formula can be summarized by $I_i = n_i \Phi A S$, with $S = \sigma_i \theta \lambda_i y_i T$ the atomic sensibility factor.

For the chemical analysis, one is interested in the relative concentrations, so we get a composition ratio then:

$$\frac{n_1}{n_2} = \frac{I_1/S_1}{I_2/S_2}$$

The values of S can be found in tables for the instrument in question.

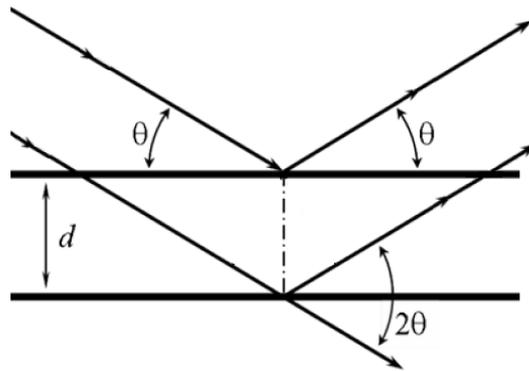
A generalized expression for determination of the atomic percentage is:

$$C_1 = \frac{n_1}{\sum_i n_i} = \frac{I_1/S_1}{\sum_i I_i/S_i}$$

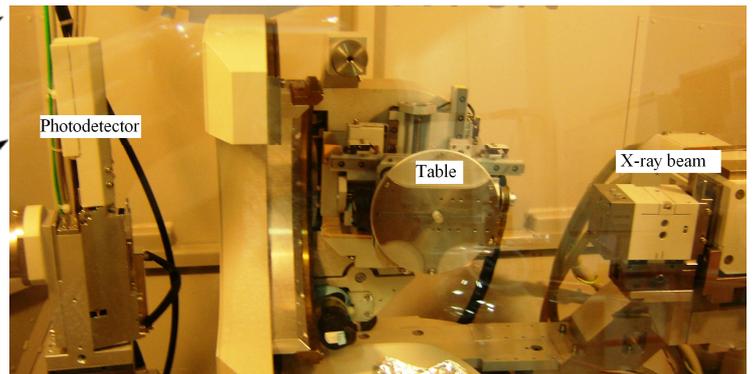
With this formula it is possible to determine the stoichiometry of the sample. In the energy spectrum is also a certain intensity ratio between the lines of the same element, this ratio occurs from the degeneracy of the total angular momentum.¹⁸

2.4 X-ray Diffraction (XRD)

In this technique the material is also irradiated with X-rays like in XPS but now the X-rays enter under a variable angle called θ . Most of the incoming waves will be scattered from the surface (see figure 10a), however some will be absorbed. Depending on the angle with the crystalline plane, there will be destructive and constructive interference between waves reflected from adjacent planes. For constructive interference the following formula called the Bragg law²⁰ holds: $n\lambda = 2d \sin \theta$ where n is the order of diffraction (integer), λ the wavelength of the X-rays, d the spacing between the planes and θ the diffraction angle.



a.



b.

Figure 10: a) reflection on planes and b) the XRD apparatus

In figure 10b there is a photo of the XRD apparatus. From the left comes a beam with X-rays ($\lambda = 1.5418 \text{ \AA}$), which will irradiate the sample on the table. On the right, the intensity of the scattered waves is measured by a photodetector. Before starting a measurement, we first have to align the sample with the diffractometer; this is done by changing the offset of z - and ω -values. During the measurement, the table is rotated over θ which results in different intensities of scattered waves. The results are shown in a graph of 2θ against the intensity. If there is constructive interference, a peak appears and from its position the spacing d between the layers can be determined.

Not only the spacing can be determined, also the size of the coherently diffracting domains of the crystal can be deduced. This is done by measuring the width of the peak, the relation is shown in the Scherrer formula²¹:

$$L = \frac{0.94\lambda}{B \cos(\theta/2)} \text{ where}$$

L is size of the coherently diffracting domains of the crystal along the c-axis,
 λ the wavelength of the X-rays,

B the width of the peak in radians, so $B = \frac{\pi}{180^\circ} \Delta\theta$

θ is the diffraction angle of the peak, but here divided by 2.

3. EXPERIMENTAL METHOD

In this experiment we tried to intercalate four different molecules into graphite-nitrate. For each molecule a specific method is used, so a short description of these methods is given in the following.

C₆₀

There are two methods used for intercalation, one where the process takes place at a temperature above the room temperature (method 1) and another one for insertion at room temperature (method 2).

Method 1:

Initially we made a solution of 15 mg graphite-nitrate in 100 mL toluene and let this reflux for four days. Figure 11 shows the set-up for the reflux, this technique involves condensation of the vapour in the boiling flask and this condensate returns back to the system. For the heating an oil bath was used, this was held at a constant temperature of 53 °C. After this we solved some fullerene (powder) in toluene and sonicated this solution, to favour fullerene dispersion in the solvent. Then the two solutions are mixed and refluxed again for three days.

To get rid of any kind of not reacting graphite-nitrate and fullerene we washed the solution three times with the help of a centrifuge at 4500 rpm for 25 minutes at room temperature. After the centrifugation most of the intercalation compound will remain on the walls. After the first centrifugation we refilled the bottles with toluene and used the centrifuge again. In the end the powder solved in a bit toluene (less than 5 mL) can be cast on a Petri dish. The remaining solvent evaporates and only the powder remains.

Method 2:

This method is similar to the first one, only without heating.

Ethylene Glycol

For intercalation of this molecule we also used various methods. We started with an evaporation method concerning only the powder and the liquid molecule. For this we put some graphite-nitrate powder in the middle of a bottle and dripped three drops of ethylene glycol against the walls. This bottle was put in the oven, which is at 60 °C, for 2.5 hours. After this time the powder had to cool down to room temperature. We repeated this evaporation method with the oven at 40 °C and 45 °C and left it there for 4 hours.

In the second method we first prepared a substrate with graphite-nitrate on it. This is done depositing some layers of graphite-nitrate, for that we first made a dispersion of graphite-nitrate in toluene. This solution is dropcast onto the substrate to get one layer, for more layers this procedure was repeated. Finally we put the prepared substrate in the middle of

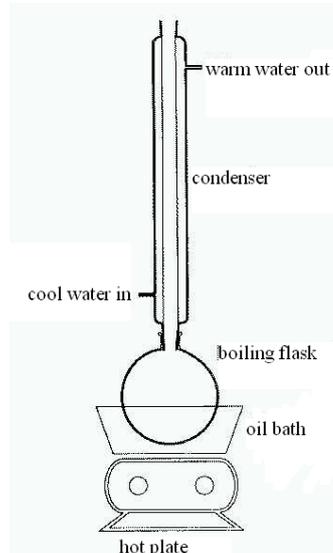


Figure 11: reflux set-up

a bottle and again dripped some drops of ethylene glycol against the walls. This bottle is placed in the oven at 55 °C for 4 hours and afterwards cooled down to room temperature.

Cyclohexane

For the cyclohexane we used again the evaporation method (analogous to the first method described for ethylene glycol), this time with the oven at 45 °C.

Adamantane

For this molecule we did the same as in the second method used for C₆₀. In the end, too little powder remained, so we repeated this procedure with double the amount of graphite-nitrate and adamantane.

All these methods gave us some powder; for each compound this powder was dispersed in toluene and dropcast on a substrate. The layers are dried with argon to accelerate the evaporation of the toluene. As substrate for the XRD we used a silicon wafer covered by silicon oxide (SiO₂/Si) and for XPS a polycrystalline gold film deposited on mica. The XPS substrate is flame-annealed after deposition of the Au film to obtain a flat surface.

4. RESULTS

4.1 Graphite-nitrate

The starting material for intercalation in this experiment was graphite-nitrate. To determine if intercalation has occurred, the lattice spacing along the c-axis of graphite-nitrate has to be determined. This is done by XRD and the result of this measurement is shown in figure 12. From this graph we determine the position of the peaks and also the full width at half maximum of the most intense peak.

First the crystalline form is determined; the third peak (003) appears at $2\theta=26.79\pm 0.05^\circ$, given that the wavelength (λ) is 1.54 \AA , by using the Bragg law we get that the spacing between the layers (d) is $3.32 \text{ \AA}\pm 0.01$. We want to find the lattice constant d_i , for this we first need the identity period, which we get from multiplying this result by three, this gives. $I_c = 9.96 \text{ \AA}\pm 0.03$. This multiplication can be explained by looking at the miller indices, as seen in figure 13, the (003) indicates that the z-axis is crossed at $1/3$ based on a cube with edges of length one. In the theory the formula of the identity period was already given, $I_n = d_i + 3.35(n - 1)$ and we know that we have a stage 2 graphite-nitrate, so $d_i = 6.61\pm 0.03 \text{ \AA}$.

Now the Scherrer formula is used, the broadening (B) of the (003)-peak is

$0.51\pm 0.05^\circ$. This is $\frac{\pi}{180^\circ} \cdot 0.51^\circ = 0.0089\pm 0.0008$ in radians and gives a size of the coherently diffracting domains of the crystal along the c-axis of about $163.8\pm 16.5 \text{ \AA}$. This corresponds to about 15 to 18 identity periods.

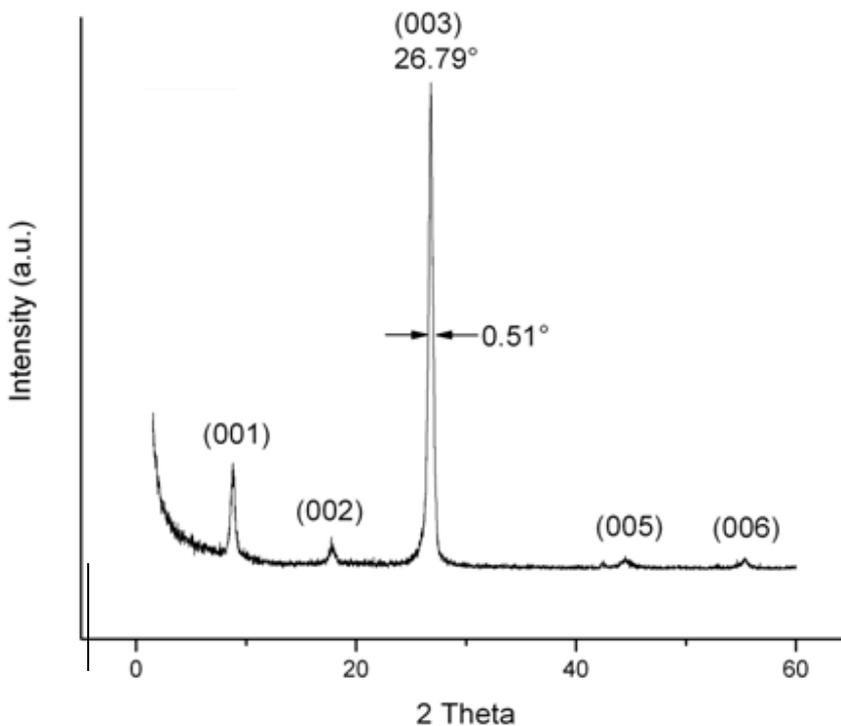


Figure 12: XRD of Graphite-nitrate

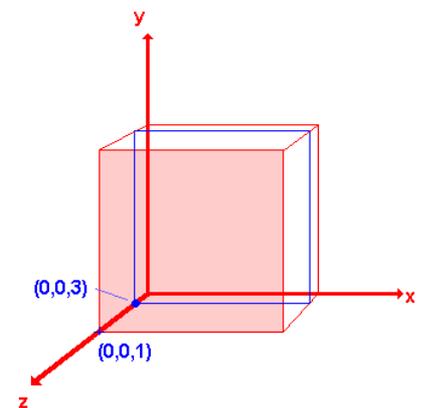


Figure 13: visualization of the used miller indices

In figure 9 the XPS of graphite-nitrate and the detailed peak of the C1s-core level region were already shown. In the C1s-core level region (figure 9b) three contributions can be distinguished,²² namely that due to the C-C bonds of graphite at 284.4 ± 0.1 eV binding energy which account for 90% of the total C1s intensity; a second one assigned to C-O, C-N bonds at a binding energy of 286.0 ± 0.1 eV and finally the one due to C=O bonds at a binding energy of 287.7 ± 0.1 eV. The latter two components are indicative of the interaction of the nitric acid groups with the graphite.

The nitrogen atoms are not clearly seen in the overview scan. In figure 14 the detailed scan of the N1s-core level region is shown. At 407.2 ± 0.1 eV binding energy we find the contribution due to the nitrate groups, the intercalated molecules. The three other peaks are associated with different chemical groups containing nitrogen,²³ namely the protonated amines (401.5 ± 0.1 eV); free amines (399.3 ± 0.1 eV) and carbon bound to nitrogen (397.9 ± 0.1 eV). These compounds are formed in reactions of the nitric acid with the graphite during the intercalation.

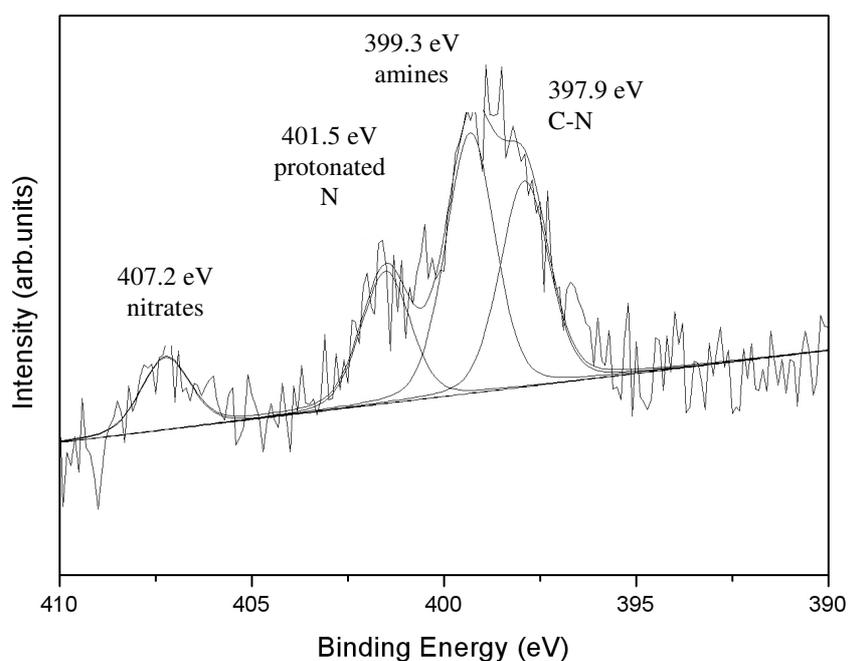


Figure 14: N1s-core level region of graphite-nitrate

4.2 Graphite-nitrate intercalated with C₆₀

The first molecule tried for intercalation was C₆₀; for achieving intercalation we used two methods: one at a temperature above the room temperature (method 1) and another one at room temperature (method 2). The first method did not give the expected results since the XRD spectrum after intercalation was that of pure graphite, probably because the temperature was too high so that the nitrate-groups de-intercalated. The result of the material produced with the second method clearly indicates that this approach was successful. This is demonstrated by the XRD data collected at various temperatures while heating the compound from room temperature to 125 °C, as shown in figure 15. At room temperature there is a clear peak around $2\theta=9^\circ$, by heating this peak disappears, so this peak is caused by the nitrate groups. At a temperature above 75 °C, we see that there is a broad peak around $2\theta=9.5^\circ$, this was not seen clear in the XRD at room temperature.

First we have to check if this peak is not caused by fullerene itself, so we also made a XRD of C₆₀, this is shown in figure 16. In this figure also the detailed peak around $2\theta=10.8^\circ$ is shown. In the detailed scan it is showed that there are three peaks here lying close to each other; one with a very high intensity and two with a lower intensity, a couple of these peaks are characterized.²⁴ The peaks of the fullerene occur at angles starting from 10.5° , the peaks in the intercalated compound occurred around an angle of 9.5° (see figure 15). Now we can conclude that this broad peak in the temperature dependent XRD was not caused by fullerene on the surface. We can therefore assign it to intercalated C₆₀ molecules, from this we can use that the broad peak appears at $2\theta=9.7\pm 0.1^\circ$ and thus the spacing is $9.1\pm 0.1 \text{ \AA}$.

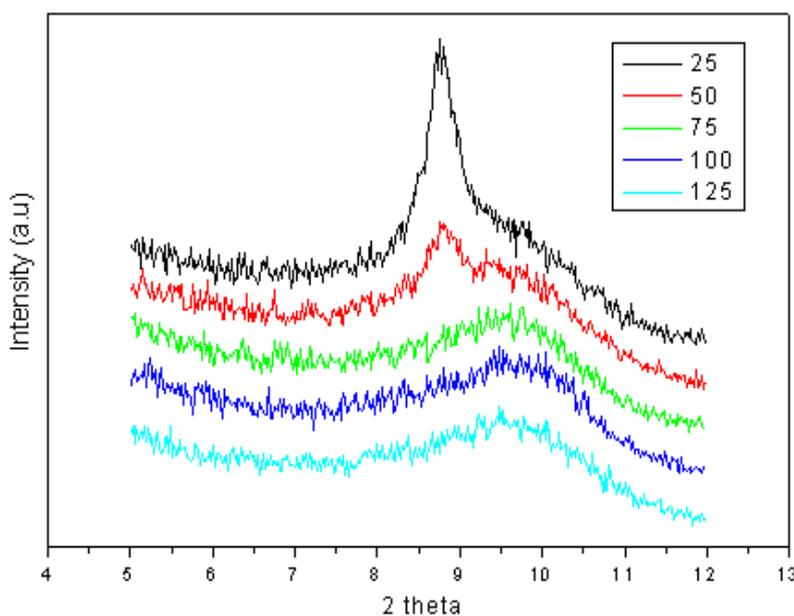


Figure 15: XRD of graphite-nitrate C₆₀ in 25, 50, 75, 100 and 125 °C

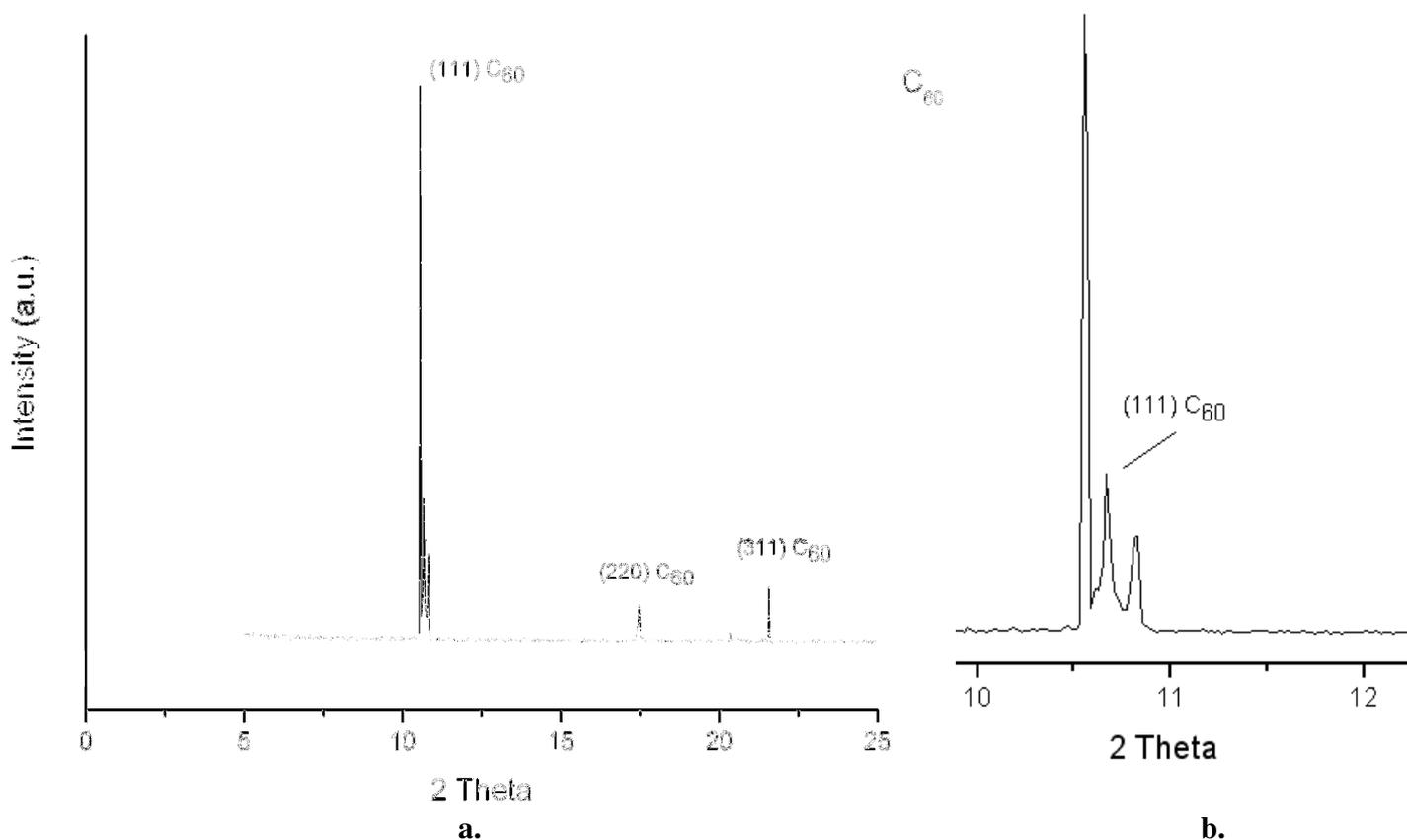


Figure 16: XRD of C_{60} with characterization of the peaks a) overview and b) detailed peak around 10.8°

Now that we have established that intercalation of C_{60} has occurred, it is important to establish how the molecules are bound to graphite-nitrate. For this we collected XPS spectra of the intercalated compound, presented in figure 17. In figure 17a the C1s-core level photoemission spectrum of unheated graphite-nitrate C_{60} is shown, the form of the peak can be decomposed into several smaller peaks. At 284.4 eV binding energy we find the contribution of the C-C bonds of graphite, at slightly higher binding energy (285.3 eV) is the peak associated to C_{60} with the associated shake-up structures at 288.9 eV and 291.0 eV. In addition we can identify the contributions due to chemical groups formed during nitrate intercalation, C-O and C-N at 286.7 eV and C=O at 287.6 eV binding energy. Quantitative analysis of the spectrum tells us that C_{60} corresponds to approximately 30% of C1s signal of intercalated in the graphite-nitrate. In figure 17b we present the C1s core level photoemission spectrum of the same C_{60} intercalated graphite-nitrate after heating to 75°C , again together with the result of the fit. In this figure, the largest peak stems from the intercalated C_{60} and the graphite itself. The other peaks at higher binding energy are the shake-ups of C_{60} . Because of the heating, the weak bonds between the graphene and nitric acid molecules break up and nearly all the nitric acid deintercalates. The fullerene molecules instead remain and act as robust pillars between the graphite planes. In figure 17c the XPS spectra of the N1s-core level region of graphite-nitrate is shown and in 17d the corresponding spectrum of graphite-nitrate intercalated with C_{60} . By comparing these two spectra we can see that the peak of the nitrate

molecules (around 407.2 eV) is reduced. This means that during the intercalation some nitrate groups de-intercalated while the C₆₀ molecules intercalated. We also collected a XPS spectrum of the N1s-core level region after heating, but found no spectroscopic evidence of nitrogen anymore.

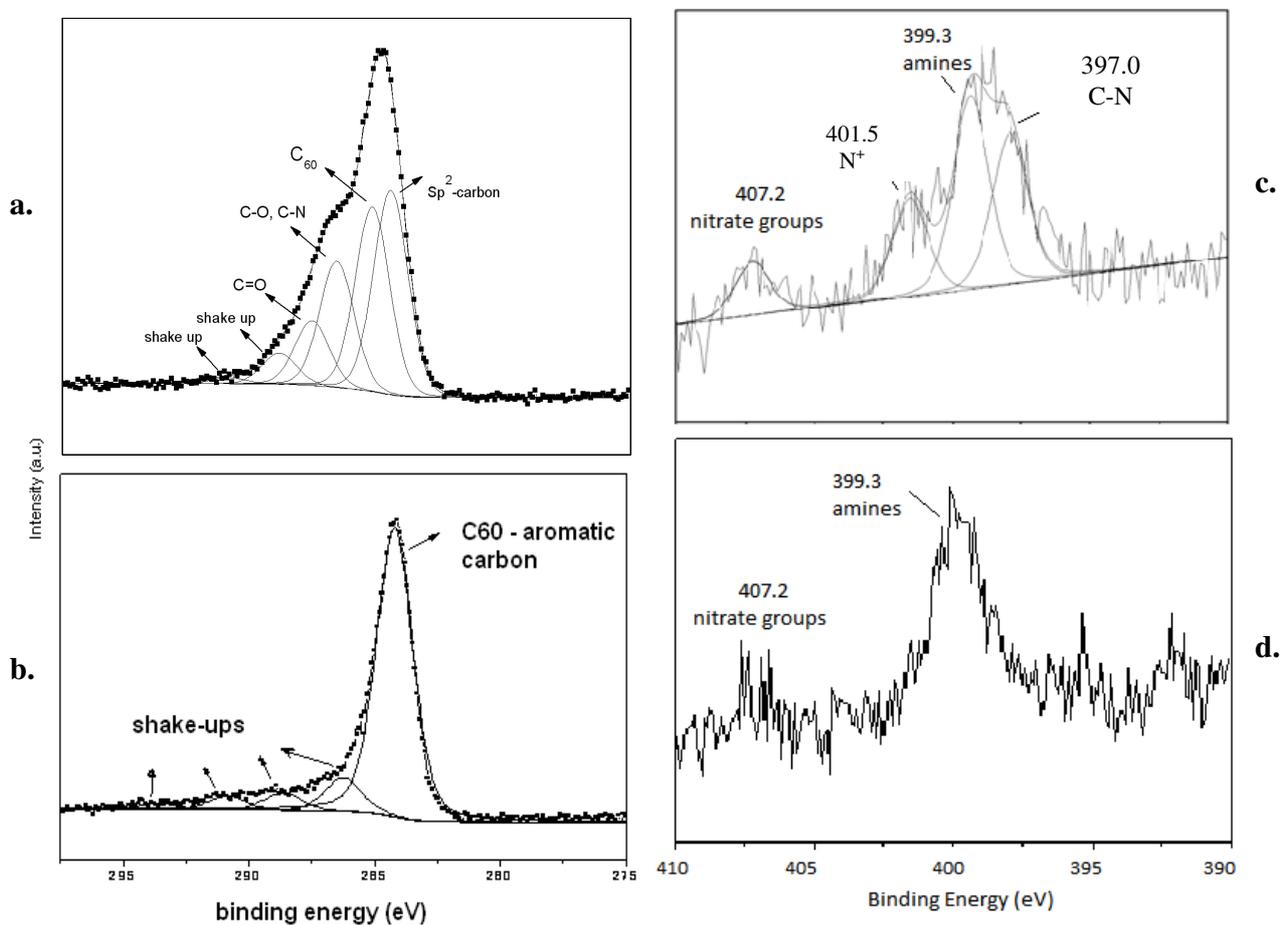


Figure 17: XPS of graphite-nitrate C₆₀ a) graphite-nitrate C₆₀ around the C1s-core level region unheated and b) graphite-nitrate C₆₀ around the C1s-core level region heated and c) graphite-nitrate around the N1s-core level region unheated and d) graphite-nitrate C₆₀ around the N1s-core level region unheated

4.3 Graphite-nitrate intercalated with ethylene glycol

In figure 18 the XRD results of the compound resulting from our intercalation attempts with ethylene glycol are shown together with those of the starting material. For this intercalation we used two methods as explained in chapter 3. The first method was used at different temperatures but in the figure only the result for 45 °C is shown since the other temperatures gave the same result. By comparing the data for the compound resulting from intercalation of ethylene glycol (blue) with those of the starting material (red), we see that they are almost the same. The only difference is the intensity of the peaks at the angles higher than 40 degrees. Hence the conclusion is that intercalation did not occur. The product of the second method (green line) does not show any diffraction peaks and therefore this method did not produce the desired outcome.

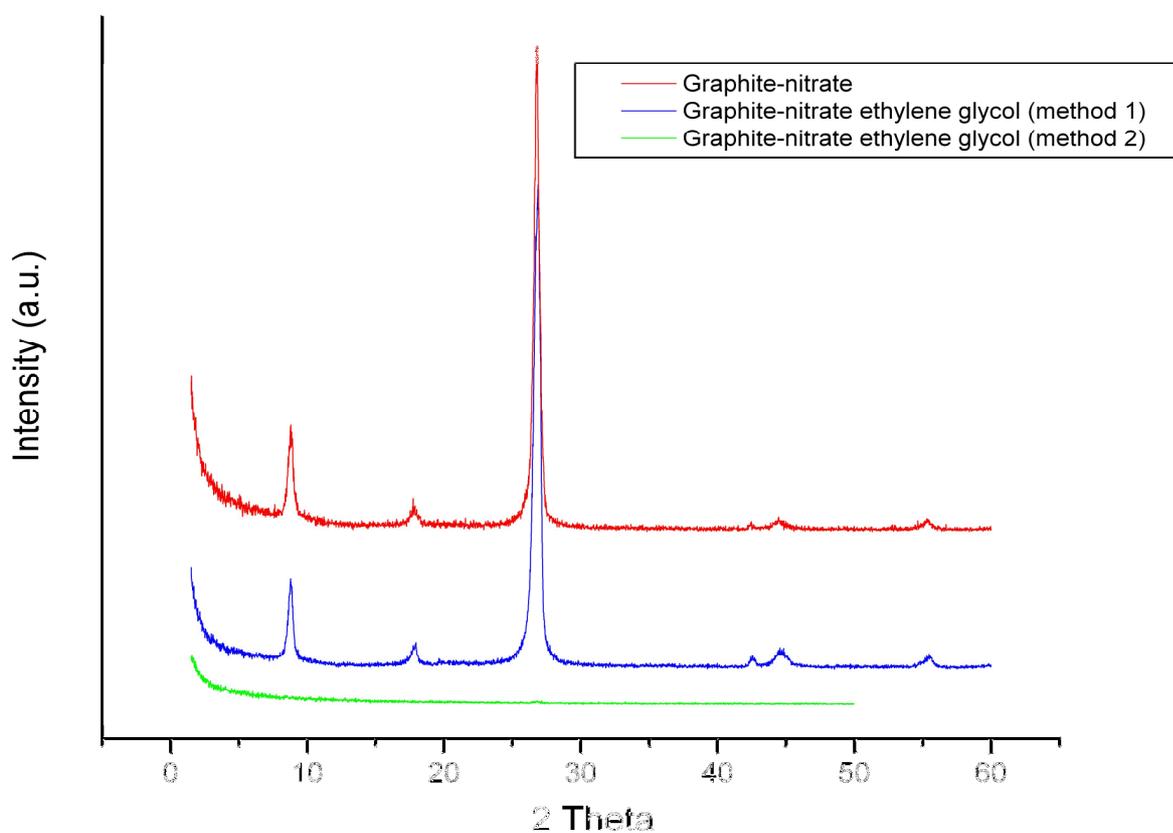


Figure 18: XRD of graphite-nitrate ethylene glycol

4.4 Graphite-nitrate cyclohexane

In figure 19 the XRD data of the compound resulting of the intercalation attempts of cyclohexane into graphite-nitrate are shown together with those of the starting material. There is almost no difference, the peaks at the higher angles disappeared and the intensity of the graphs differs. However, the angles where the peaks occur in those graphs are the same, so the spacing did not change and we can conclude that no intercalation occurred.

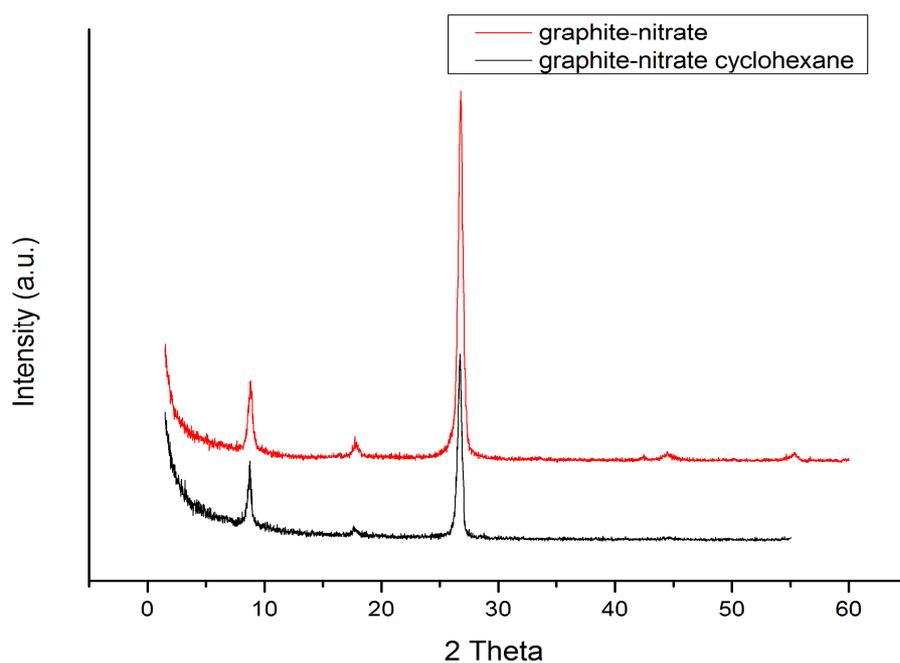


Figure 19: XRD of graphite-nitrate cyclohexane

4.5 Graphite-nitrate adamantane

In figure 20 the XRD data of graphite-nitrate after intercalation with adamantane are compared to those of the starting material. The compound obtained after intercalation shows extra peaks at angle lower than 7.5 degrees: two intense peaks correspond to spacings of $20.05 \pm 0.03 \text{ \AA}$ and $13.9 \pm 0.04 \text{ \AA}$ and the weak peak to 10.0 \AA . The first explanation could be that adamantane molecules have crystallized on the surface of the graphite-nitrate; to confirm or dispel this hypothesis, a diffraction pattern of adamantane was taken as displayed in figure 21. This sample was prepared in the same way as the other samples, namely by dispersing the powder in toluene and dropcasting the dispersion onto the substrate. In this graph no diffraction peaks at angles lower than 4 degrees are seen, so we can conclude that these features in the pattern of the intercalation compound are not due to crystallites of adamantane. Therefore we conclude that a reaction with the nitrate molecules inside the graphite must have occurred and therefore intercalation has been successfully achieved resulting in an enlarged spacing.

Also for this sample we investigated what happens when the sample is heated to the temperature where the nitric acid molecules de-intercalate. In figure 22 the results of a temperature dependent XRD are shown. Here we can observe that at 50°C the peak at 20.05 \AA starts to disappear and when the sample is heated to 75°C , the whole diffraction pattern disappears (the graphite peak at about 26° is outside the scale of this graph), suggesting that both nitrate and adamantane molecules de-intercalate at this temperature.

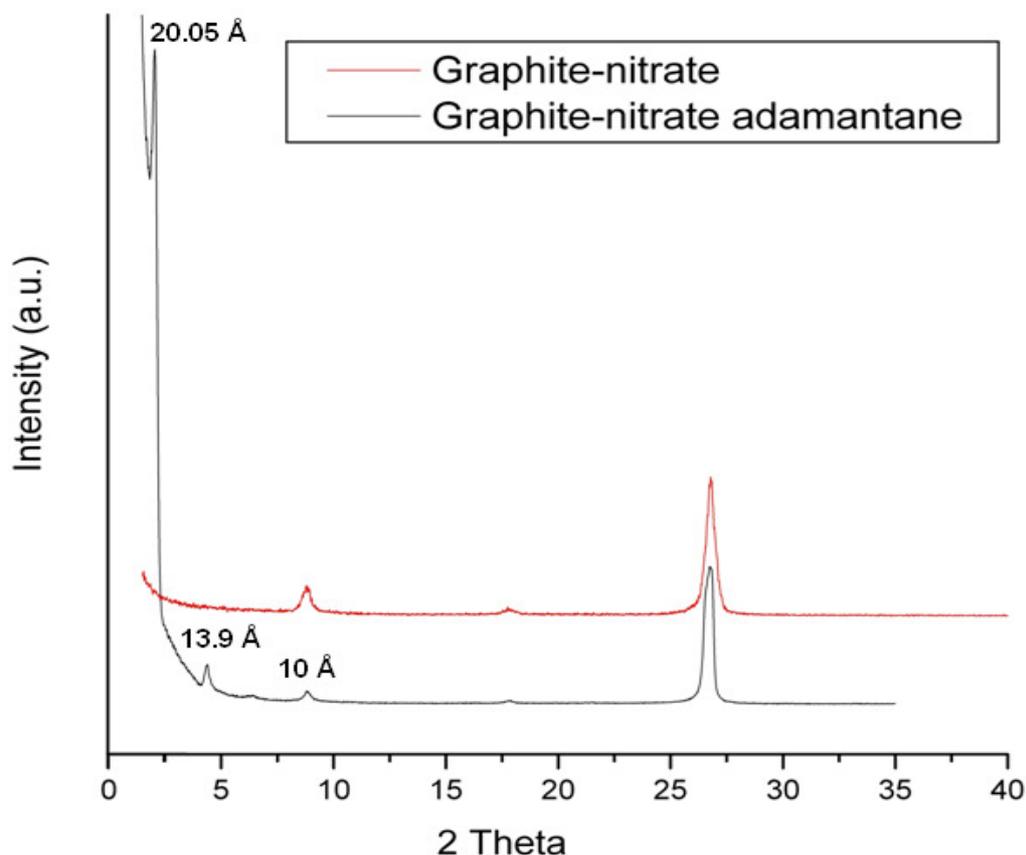


Figure 20: XRD, intercalation of adamantane into graphite-nitrate

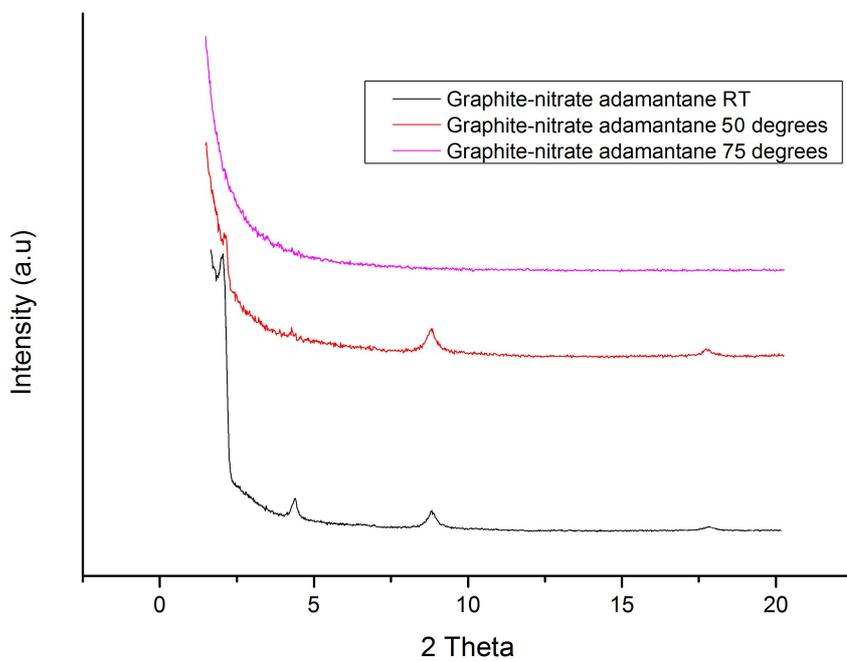
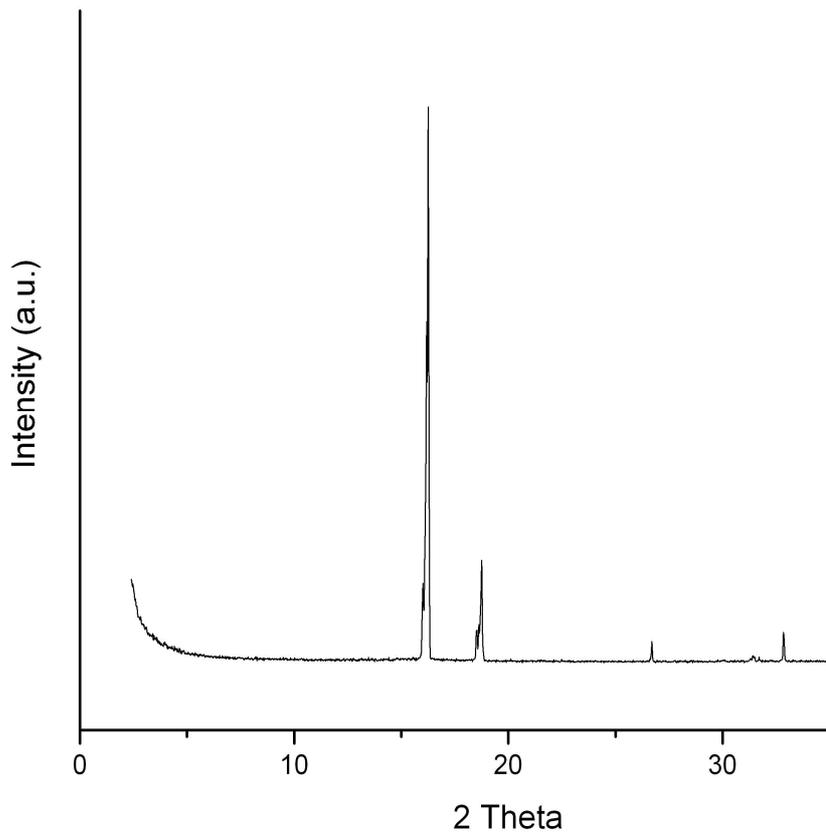


Figure 22: Temperature dependent XRD of graphite-nitrate intercalated with adamantane

5. DISCUSSION AND CONCLUSION

Our aim in this project was to determine if intercalation occurred for C₆₀, ethylene glycol, cyclohexane and adamantane. This was done by determining the spacing between the layers of the intercalation compounds by using XRD and comparing the results with the structure of the starting compound.

The lattice constant (d_i) of the starting compound was calculated to be 6.61 ± 0.03 Å, which corresponds to the β -crystalline form. In addition, the size of the coherently diffracting domains was determined by using the Scherrer formula; this gave us a size of 163.8 ± 16.5 Å, this corresponds to about 15 till 18 identity periods. The composition of graphite-nitrate was checked by XPS.

In the case of C₆₀ successful intercalation into graphite-nitrate was achieved. In fact, a spacing of 9.1 ± 0.1 Å was determined. From the literature we know that the diameter of C₆₀ is 7.1 Å, so we were expecting something higher if intercalation occurred because also the Van der Waals radius is involved. It was only possible to see the intercalation after heating the compound. From the XPS we saw that intercalated C₆₀ made up about 30% of the C1s intensity. From the XPS data collected after heating the compound to a temperature where we know that nitric acid de-intercalates, we can conclude that C₆₀ remains between the graphite sheets when nitric acid leaves the interlayer space and that the fullerene acts as robust pillars between the graphene planes. In a next experiment one could determine the best ratio between the molecule and graphite-nitrate to get the optimal intercalation compound.

Two other molecules tried for intercalation where ethylene glycol and cyclohexane, but both did not give successful results. This has to do with the polarity of the molecule, we know that ethylene glycol is a polar and cyclohexane is non-polar. Nitric acid is a polar molecule, we tried to intercalate ethylene glycol by evaporation to check if it would attach to the nitric acid. We did the same for a non-polar molecule cyclohexane to check if it bonds to the graphene sheets. So probably these molecules do not intercalate into graphite-nitrate.

Intercalation was also achieved for adamantane, here we found a spacing of 20.05 ± 0.03 Å and 13.9 ± 0.04 Å. Now we need to understand how the molecules have bonded to graphite-nitrate. The size of one adamantane molecule is about 9 Å (see chapter 2.2.4), so the spacing seems to be very large. A possible configuration that might cause such a diffraction peak could be a short chain of one nitrate and one adamantane molecule, which gives a spacing about 14 Å. If such chains are arranged in a tilted fashion, a correspondingly shorter spacing should result. Another possibility is that a chain of two adamantane and one nitrate molecules is formed between the graphene layers²⁵, which should give a spacing about 20 Å. In the temperature dependent XRD we already saw that both the nitrate and adamantane molecules de-intercalate. We already know that the nitrate molecules de-intercalate at temperatures above 75°C, an explanation why both molecules escape at the same temperature, is that these two molecules are bond together. For checking this hypothesis XPS-spectra would be very useful but could not be measured due to technical problems with the equipment which could not be solved within

the deadline of this project. Since nitric acid does not bind covalently to either C_{60} or graphite, we also propose another arrangement which also could give rise to an enlarged lattice spacing and which involves adamantane molecules interacting with the upper and the lower graphene plane in the presence of nitric acid in the interlayer space as sketched in figure 23. This configuration should result based on the tendency of adamantane to accept charge – which would be available on the graphene planes. To discriminate between these configurations XPS and IRRAS experiments need to be performed.

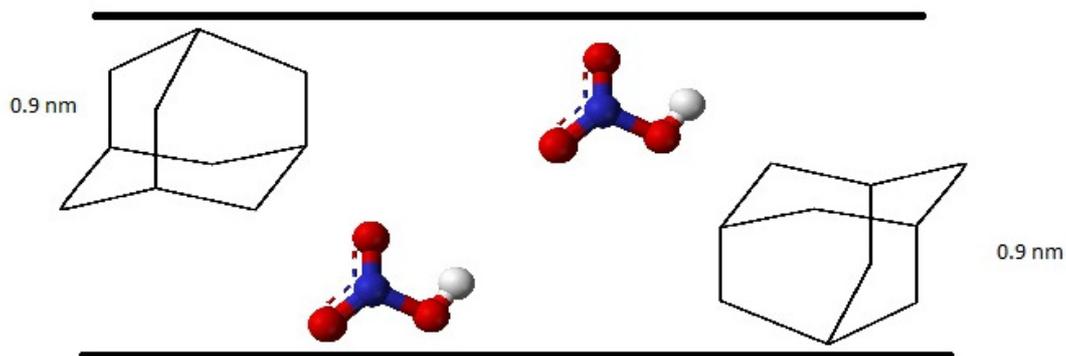


Figure 23: Proposed arrangement of adamantane when intercalated into graphite-nitrate. The thick black lines represent the graphene planes, nitric acid and adamantane are drawn with their molecular structure.

In conclusion, we only achieved intercalation for C_{60} and adamantane, the reasons why the other two molecules did not work are not clear at the moment and call for further research on other candidates intercalation to establish a trend.

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