Refractive index for sulfur S$_8$ molecules between graphene layers and inside graphite

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Abstract. The refractive index for sulfur molecules adsorbed between graphene layers, and inside graphite is calculated. We remark some noticeable differences between the periodic system along the perpendicular direction to the graphite layers, and the system used to study a lonely sulfur molecule in interaction close to an isolated graphene layer. We obtained -0.00914 eV for the adsorption energy per sulfur atom when one S$_8$ molecule is relaxed by means of self-consistent calculations (scf), and variable cell calculation (vcc), between two graphene layers, but we got a big positive energy 11.4954 eV for the possible insertion of the S$_8$ molecule between a pair of more separated graphite layers, A and B (c = 7.7978 Å).

1. Introduction

We investigate the adsorption of the sulfur coronene molecule S$_8$ for two kinds of systems formed with graphene or graphitic layers. We give similarities and differences in the optical properties of the studied systems. The refractive index is calculated by means of density functional theory. The first system to be studied formed by one or two equivalent graphene layers with big or small distance in-between will be denoted as C32S8, this is formed by graphene layers with 32 carbon atoms plus the coronene S$_8$ sulfur molecule. Big distance in-between gives results for adsorption on an isolated graphene layer, small distance in-between is to study the effect on the adsorption of the sulfur molecule when there is a pair of close equidistant graphene layers to the molecule. The second system, denoted by AS8BS8 is like C32S8 but with the graphene layers replaced by nonequivalent graphitic layers A and B, as in graphite. Then, there is a sulfur molecule between any pair of layers in the periodic system ABABAB. This ab initio computational study explains some of the experimental results for the sulfur interaction under thermal treatments between graphene layers.

2. C32S8 system. Electronic band structure.

To design the equilibrium configuration of the coronene molecule S$_8$, we used the information given by Meyer [1]. To calculate the refractive index of the systems briefly mentioned before, we made use of a computer code such as Quantum espresso [2] to obtain within the DFT (density functional theory), the necessary elements to build the optical properties. Among other possibilities, we preferred to work with...
norm conservative pseudopotentials C.pbe-hgh.UPF and S.pbe-mt_fhi.UPF, respectively for both, C and S atoms, to preserve the charge and reduce the time for the computer calculations. First, by a pair of independent computer relaxations, equilibrium optimized configurations were obtained for the graphene layer and for the S8 molecule. Next, the sulfur molecule was placed above a lonely graphene layer and the entire system was relaxed. Two self-consistent calculations done for the final coordinates of the sulfur and carbon atoms, allows to obtain the small physisorption energy of -0.04165 eV for the sulfur molecule on the graphene layer. Because the system has 40 atoms, the adsorption energy per atom is only -0.001041 eV. The adsorption energy is obtained using equation (1)

\[ E_{ad}(S_8) = E(S_8 \text{ on gl}) - E(\text{gl}) - E(S_8) \]

\( E(S_8 \text{ on gl}) \) is the total energy for the relaxed system formed by one S8 molecule and the graphene layer (gl), \( E(S_8) \) is the total energy of only the sulfur molecule in the final configuration and in a similar way, \( E(\text{gl}) \) is the total energy of only the carbon atoms of the graphene layer in their final positions corresponding to the final stage of the relaxation of the entire system. In the final configuration, figure 1, periodicity is shown. Sulfur atoms closely maintain the initial coronene form, and are well above the graphene layer between approximately 4.20 and 5.18 Å. There is enough free space around the sulfur molecule to avoid possible interactions between them. The supercell parameters are \( a = 9.8380 \) Å and \( c = 20.7919 \) Å. After the self-consistent calculations of the entire system for the equilibrium configuration obtained at the end of the variable cell calculation, a trajectory with 100 k points were selected joining the high symmetry points K-\( \Gamma \)-M-K of the reciprocal cell. The band structure obtained for the system is shown on figure 2 (left side). Figure 2 (right side), show the band structure for pristine graphene. Comparing these two figures, the linear dispersion relation is seen around the K reciprocal point in both cases. This is a consequence of the small binding energy in the system. In the next section we give analogous results but for the system AS8BS8.

**Figure 1.** Configuration of C32S8 system.

**Figure 2.** Electronic band structure of C32S8 system (left panel). Electronic band structure for a pristine graphene layer (right panel).
3. AS8BS8 system. Electronic band structure.

The carbon layers of this system are a pair of non-equivalent graphite layers, A and B. Given in advance some of the principal results, we mention that the sulfur molecule becomes a planar set of atoms if the cell parameter of graphite, 6.708 Å, is used and maintained fixed in the calculation for the AS8BS8 system. Some other different cell values were also studied, the biggest one was 12.5 Å. Here we present results for a variable cell relaxation calculation of the AS8BS8 system when an initial c = 6.708 Å cell parameter is used. This value is for experimental graphite. Because the initial confinement of the two sulfur molecules is very restrictive, there are many forces on practically all the 64 carbon atoms and the 16 sulfur atoms of the unit cell. As the variable cell calculation goes on, the forces on each one of the atoms is reduced drastically in such a way that at the end of the relaxation, after 198 steps, the total force is 0.026658 and the total scf correction is 0.0. The final parameter is c = 7.7978 Å. In the final configuration there are some S-S bonds and more S-C bonds. The graphitic layers become corrugated and sulfur atoms lays approximately in the middle plane between the graphitic ones. This is shown in a periodic view of the system in figure 3. The same trajectory with 100 k points were considered, as for the C32S8 system to calculate the band structure energy, and the adsorption curves shown in figure 5.

There are some recent efforts to improve the calculation of the adsorption energy on transition metal surfaces based on DFT calculations [6]. Because the studied system is in principle simpler than metallics, it was valid to calculate the adsorption energy with equation (1). The same basic equation is used for example in reference [7], where a DFT study is done for NO adsorption on pristine graphene. There are many other works where use is made of that expression to calculate the adsorption energy. In last instance, its validity is supported by the good correspondence between calculated and experimental results for the calculated adsorption energy in all those systems.

4. Refractive index of C32S8 and AS8BS8 systems.

In this section we cite some basic expressions used to calculate the reflectivity in terms of the refractive index, among other optical properties. The electronic band structure (on the edge of linear optics) plus the formalism RPA (random phase approximation), let us calculate the imaginary component of the dielectric tensor. The real component is obtained making use of Kramers-Kronig equations [4,5]. The optical response to electromagnetic waves, through the material, is known after the knowledge of the imaginary component of the dielectric tensor. The reflectivity at normal incidence (equation 4 of reference [3]), depends on n and k, the real and imaginary part of the complex refractive index, also known as refractive index and extinction coefficient, respectively. Both terms depend strongly on the dielectric tensor, as shown in equations 5 and 6 of reference [3]. Also, the absorption coefficient was calculated in terms of k. Once the electronic band structure has been calculated, the optical properties of the systems studied in this work can be calculated executing the epsilon.x postprocess executable application of quantum espresso computer code. In this way the absorption for G (isolated graphene layer), GS (graphene layer with the S8 molecule physically adsorbed on the graphene layer), and GSG systems were calculated. The GSG system is formed by a pair of graphene layers with the S8 molecule between them. Infrared, ultraviolet, and visible adsorption curves were obtained and are compared for those
systems. Also, the reflectivity curves were calculated. Figure 4 shows those results. In each panel of the figure, there are three different curves: dashed line for graphene layer, dashed-point line for graphene layer and sulfur molecule and points line for the sandwich system, graphene layer-sulfur molecule-graphene layer. The corresponding systems and curves can be identified by the acronyms G, GS and GSG.

Figure 4. a) Infrared, b) ultraviolet, c) visible adsorption and d) reflectivity curves. Dashed line for isolated graphene layer (G), dashed-point line for graphene layer with the S8 molecule physisorbed on the graphene layer (GS), and points line for the sandwich system, graphene layer-sulfur molecule-graphene layer (GSG).
5. Results and discussion.
The adsorption of the coronene molecule above the isolated graphene layer is very small. Even this, it can be appreciated little changes in S-S bond lengths and angles respect to the equilibrium configuration.

![Graph showing infrared, ultraviolet, and visible adsorption curves](image)

**Figure 5.** Infrared (up panel), ultraviolet (middle panel) and visible adsorption curves (bottom panel). This is the contribution of only the carbon atoms in the graphene layer-sulfur-molecule graphene layer (GSG) system.
There are also some changes between the electronic band structure for the equilibrium configuration of the C32S8 system for the isolated graphene layer, in other words, when there is a big distance between the pair of graphene layers, respect to the electronic band structure for a pristine graphene layer; these changes can be seen for example around the Γ point of both bands of figure 2. Next, we give some comments about optical properties of the C32S8 system. In the infrared and visible region, the absorption is small for graphene (G), increases for GS and is bigger for GSG system. Apparently, the major contribution in the ultraviolet region comes from the GS system, below $1 \times 10^5$ (1/cm) and is the bigger one for the entire system GSG above that value. The reflectivity qualitatively has the same trend as the ultraviolet results. We don’t know any other report about optical properties of this kind of system.

On the other way, for the AS8BS8 system we give the infrared, ultraviolet and visible adsorption curves. This is the contribution of only the carbon atoms in the graphene layer-sulfur molecule-graphene layer (GSG) system. The contribution of the sulfur atoms to the adsorption in that curves is negligible compared with that of carbon. This is still under study.

**Conclusions**

It is important to emphasize that scf and vcc results for one S8 molecule between two graphene layers ends with a final c parameter of 8.8572 Å, with -0.00914 eV for the adsorption energy per sulfur atom. If the molecule is confined by graphite layers A and B (initial parameter c = 6.7080 Å), the vcc result shows a final parameter c = 7.7978 Å and the new configuration is shown in figure 3. The bonds between carbon and sulfur atoms shown in that figure confirms and agrees with experiment [8]. Sulfur is incorporated into multilayers graphene. Molecular dynamics simulations are on course to determine the desorption temperature of sulfur from the graphitic material. Those results will be given elsewhere. The studied systems could be used to capture sulfur from some sulfured materials and then by effect of temperature, desorption and release of sulfur atoms and molecules could be obtained in a controlled way. The positive adsorption energy 11.4954 eV means that in principle, an energy close to 11.5 eV will be required to introduce the S8 molecule between a pair of more separated graphite layers. On the other side we have calculated the refractive index, infrared, ultraviolet, visible adsorption and reflectivity curves for all the systems.

**References.**

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