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Dissociative adsorption of atmospheric molecules at vacancies on the graphite (0001) surface of samples exposed to plasma

A. Allouche *, Y. Ferro

Physique des Interactions Ioniques et Moléculaires, CNRS and Université de Provence, Campus de Saint Jérôme, Service 242, 13397 Marseille cedex 20, France

Abstract

The quantum Density Functional Theory (DFT) model of a single atom vacancy on the basal graphite surface is first validated through comparison of the theoretical vibrational spectra of the fully hydrogenated defect with the corresponding High Resolution Energy Loss Spectroscopy (HREELS) spectra. We then proceed to investigate atmospheric molecules adsorption on vacancy defects on the (0001) graphite surface. Carbon dioxide and nitrogen have no interaction with the defect whereas carbon monoxide is incorporated into the vacancy with an activation energy of 1.5 eV. Water dissociates with a barrier of 1.6 eV, forming an adsorbed hydroxyl radical. Molecular oxygen dissociates with a very low barrier (0.2 eV).

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1. Introduction

At present, one of the most disastrous events that can occur in nuclear fusion reactors is air invasion after a pipe break [1]. The plasma facing materials will then suffer from chemical reactions with the most abundant atmospheric gases such as nitrogen, oxygen, water and carbon dioxide. These gases reactivity will interfere with the critical problem of deuterium and tritium retention through the graphite oxidation mechanisms. Direct oxidation of the graphitic substrate produces carbon monoxide (CO) and carbon dioxide (CO_2). Molecular oxygen dissociation under plasma interaction or because of the chemical reactivity of the graphite surface defects engenders atomic oxygen which in turn can combine with the neutral hydrogen isotopes to give hydroxyl radical (OH) and water (H_2O).

Many theoretical works have been published recently about reactivity on the (0001) surface of graphite, taken as a model of carbonaceous compound. Nevertheless, this model should be considered only as a first-order of approximation and its reactivity is very low. In laboratory, models of defective surfaces are created by bombarding perfect (0001) surfaces with energetic ions beams.

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* Corresponding author. Fax: +33 4 91 28 91 94.
E-mail address: Alain.Allouche@up.univ-mrs.fr (A. Allouche).

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The reactivity of atmospheric gases on graphitic surfaces also has an important impact in the field of laboratory simulation and in the postmortem analysis of the carbon deposits extracted from the plasma facing tiles of the first wall and divertor. However, laboratory analysis is very often carried out a long time after extraction of the samples, which can consequently be polluted by atmospheric gases. Among the main techniques implemented in laboratory, vibration (Raman, HREELS) or electronic (UPS, XPS, EELS, EXAFS) spectroscopies are most often used.

In the present paper, the quantum Density Functional Theory (DFT) model of a single atom vacancy on the basal graphite surface is first validated through comparison of the theoretical vibrational spectra of the completely hydrogenated defect with the corresponding High Resolution Energy Loss Spectroscopy (HREELS) spectra. The adsorption of the most common atmospheric molecules (carbon oxides, water and molecular oxygen and nitrogen) on single vacancy defects on the (0001) graphite surface is then investigated.

2. Methods of computation

The system representing the graphite surface is a two-layer slab extracted from the $10 \times 10 \times 1$ multiple crystalline cell described elsewhere [2] and including a total amount of 356 carbon atoms. The vacancy defect (VD) results from one carbon missing in the central part of the cluster and located above a sub-layer atom.

The quantum method is the mixed quantum mechanics/molecular mechanics (QM/MM) ONIOM method implemented in the Gaussian 03 [3]. The high-level method is the spin unrestricted UB3LYP hybrid density functional associated to a moderately extended Gaussian basis set (6–31g). The vacancy is delimited by three *quantum* carbon atoms (called *vacancy carbons* in the following) among the 36 carbons included in the high-level quantum cluster, the ad-species (molecule or atoms) are also included in the high-level quantum system. The low-level system is calculated using the universal molecular mechanics force field (UFF).

The adsorption energies are calculated using the definition:

$$\Delta E^n = E[\text{graph} + n\text{H}] - E[\text{graph} + (n-1)\text{H}] - E(\text{H}), \quad (1)$$

where $E[\text{graph} + n\text{H}]$ stands for the total optimized energy of the system constituted of the graphite slab and n adsorbed H and $E(\text{H})$ the energy of the isolated hydrogen atom. The reaction energy is defined equivalently as the difference between the energy of the initial and final states.

The harmonic frequency calculation was performed on the quantum cluster, freezing the low-level system; they are weighted by an uniform scaling factor of 0.96 as before [4]. The calculated intensities correspond to infrared rules; the spectra are calculated by dressing the vibrational transitions with Lorentzian functions of height equal to the calculated intensities and width of $50\,\text{cm}^{-1}$ at half the maximum.

3. Vacancy model validation through total hydrogenation

The final structure after hydrogen saturation of the vacancy site is shown in Fig. 1. Every carbon near the vacancy is hydrogenated and adopts an sp^3-like tetrahedral configuration. The hydrogen bonding energies fall in the range of 4.8 eV at low coverage to 2.3 eV at completion of the site (Table 1). Of course, the *local* adsorption energies in a neighboring defect are not available experimentally, but Guttler et al. [5] detected a TPD peak at a temperature of 700 K Ar^+ on an irradiated graphite surface, whereas Zecho et al. [6] found the main desorption peak at a temperature of 500 K on the clean surface. Although no quantitative comparison can be proposed, this increase in desorption temperatures induced by the ion bombardment confirms

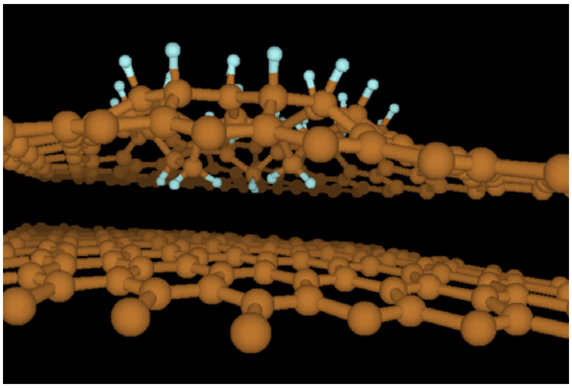

Fig. 1. Single vacancy defect structure after complete hydrogenation of the surrounding carbon atoms issued from complete ONIOM minimization of the cluster geometry (detail).

Table 1
Activation barriers and energies of the reactions studied in the text (eV)

System	Activation barrier	Reaction energy	Mechanism
H	–	From −4.8 to −2.3	Adsorption
CO_2	–	–	No reaction
N_2	–	–	No reaction
CO	1.5	−6.1	Incorporation in the graphite lattice
O_2	1.2	−3.1	Dissociation
H_2O	1.6	−1.6	Dissociation

the quantum results emphasizing the reinforcement of the CH bond.

Fig. 2 shows the evolution of the vibration spectra in the stretch modes region for three coverage rates: (i) one single hydrogen, (ii) 10 hydrogen atoms corresponds to saturation of the carbon atoms closest to the vacancy, (iii) at full saturation of the quantum part of the ONIOM system. The peak heights correspond to the infrared intensities. From (i) to (ii), the CH signal undergoes a strong down-shift from 3120 to 2870 cm^{-1}. At saturation, the signal remains approximately at the same wave-number (2850 cm^{-1}) but a new strong peak appears at 2990 cm^{-1} which is due to adsorption on carbons located at larger distance from the vacancy, their physical environment is more similar to a graphite bare surface. Therefore, comparison must be performed with the spectrum of 10 hydrogen atoms adsorbed on the carbons directly surrounding the defect.

Compared to hydrogen adsorption on clean graphite surface, the stretch and δ modes (not displayed but reported in Ref. [2]) are respectively blue-shifted by 234 cm^{-1} and 40 cm^{-1} to the values of 2870 cm^{-1} and 1240 cm^{-1}, i.e. in excellent agreement with HREELS values 2850 and 1210 cm^{-1} [5].

4. Quantum study on reactions of atmospheric molecules on vacancy defects

Carbon dioxide and molecular nitrogen have little interaction with the vacancy defect, they are only physisorbed in potential wells only 0.2 and 0.1 eV deep, respectively. On the contrary, carbon dioxide adsorbs on zigzag and armchair edges with energies ranging from 1.0 to 3.7 eV [7].

Carbon monoxide has a strong interaction (−6.1 eV) with the defective graphite surface (Fig. 3(a), Table 1). The CO's carbon atom takes the place of the missing vacancy carbon, therefore the interaction energy takes into account the three

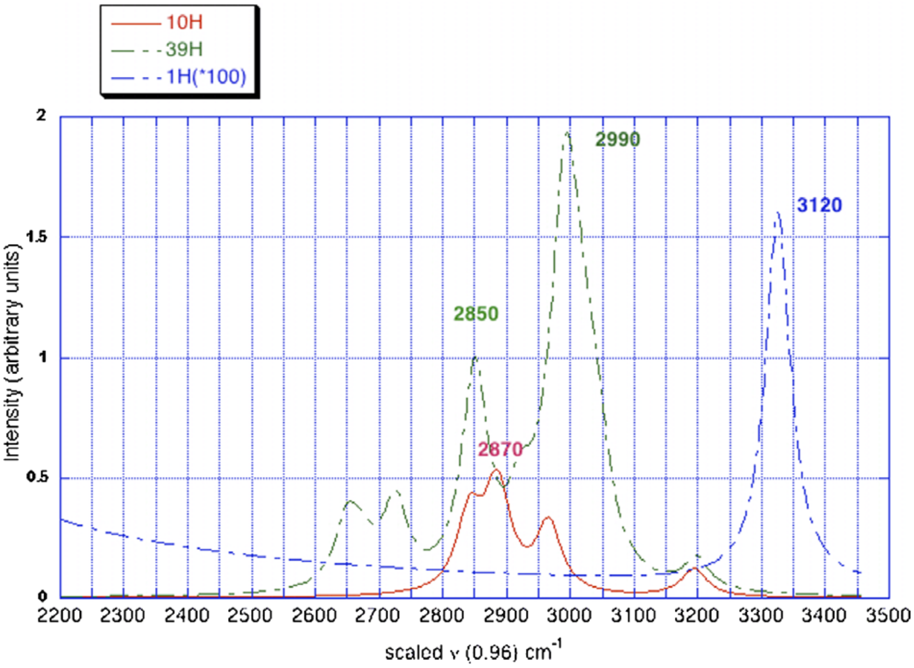

Fig. 2. Calculated vibration spectra in the stretches region of hydrogenated vacancy at various coverage rates: 1H, 10H and at saturation (39H).

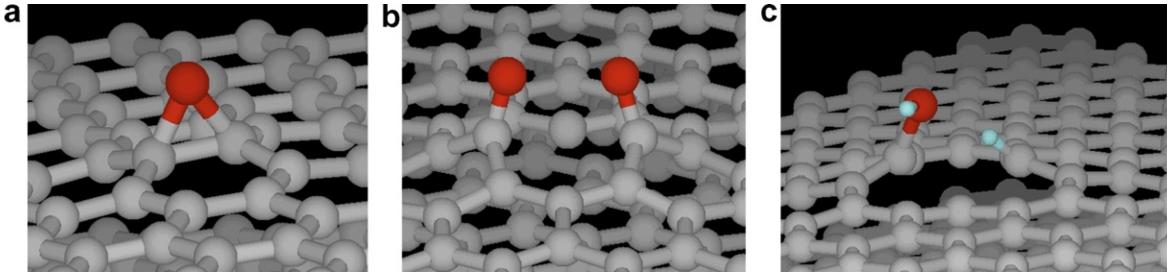

Fig. 3. Detail of the DFT calculated structure resulting from the dissociative adsorption of atmospheric molecules on the vacancy defect: (a) carbon monoxide (CO), (b) oxygen molecule (O_2) and (c) water (H_2O).

new C–C chemical bonds and the new C–O bond since the oxygen atom is in a bridging position between two carbons. On graphite surface edges, carbon monoxide transforms into ether-like structures [8].

The molecular oxygen has a triplet spin structure, therefore, it exhibits a bi-radical reactivity. The two spin parallel electrons combine with two electrons from the graphite surface broken π system to form C–O chemical bonds in breaking the O–O bond with a very low activation barrier of 0.1 eV (Fig. 3(b), Table 1). The reaction is strongly exothermic (−3.1 eV). This is in good agreement with Lee et al.'s [9] STM microscopy study of O_2 interaction with atomic vacancies created by Ar^+ bombardment.

Water also dissociates on the vacancy defect (Fig. 3(c), Table 1), but this process can nevertheless be achieved only at the expense of an activation barrier of 1.6 eV and the exothermicity is reduced compared to the former case, −1.6 eV, which is already a fairly large value. Kostov et al. [10] found several dissociative pathways with dissociation barriers from 0.7 to 2.3 eV.

5. Discussion

It follows from the former section that only carbon monoxide, oxygen and water have a significant chemical reactivity on single vacancy defects. Very recently, it has been shown that oxidation etching of graphite basal planes, but also from point defects, gives rise to monolayer-depth pits [11].

In laboratory experiments, graphite oxidation is evaluated by carbon oxides and water degassing; comparison with quantum calculations on defective graphite material is not straightforward since diffusion of gases occurs before and after reaction. It is generally accepted that the most important graphite oxidation reaction is

$$C + \alpha O_2 \rightarrow \beta CO + \gamma CO_2. \tag{2}$$

Many factors affect the rate of this reaction: temperature, oxygen concentration, geometrical factors. Moreover, graphite has a lot of pores on the inside, these pores are strewn with many defects, which form as many potential reactive sites, and the external surface to the total reaction surface ratio is only within 5% [12]. The measured activation energies then take this process into account and the experimental barriers are always non-zero: activation energies ranging from 1.8 to 2.0 eV for graphite oxidation have been measured [13] and it is actually not possible to discriminate diffusion barriers from the chemical reaction ones.

In view of the quantum results, additional chemical reactions should be introduced in the model represented by Eq. (2). Carbon monoxide produced by reaction (1) can be embedded into the graphite lattice and contribute to chemical erosion by producing adsorbed atomic oxygens. Molecular oxygen dissociates on defects and constitutes very reactive chemical sites for trapped hydrogen (deuterium or tritium), also producing water molecules. Adsorbed oxygen atoms are very reactive for trapped hydrogen producing water molecules. Water molecules, once desorbed, dissociate to produce hydroxyl radicals. Therefore, the detailed mechanism for the graphite oxidation reaction is more complicated than the suggested model and further equations should introduced:

$$\begin{aligned} &O_2(g) \rightarrow 2O(ads), \\ &O(ads) + 2H(g) \rightarrow H_2O(g), \\ &H_2O(g) \rightarrow H(ads) + OH(ads). \end{aligned} \tag{3}$$

In Ref. [10], it is reported that at high temperature (>950 °C) gas-phase dissociation of O_2, H_2O and CO_2 trapped between defective graphite layers becomes significant. The oxygen atoms thus generated are highly active and create vacancies on the basal planes. These processes can also appear, at a much larger time scale, in graphite samples extracted from the fusion chambers; spectroscopic analysis of these samples should take into account the possible trapping or reaction of atmospheric gases.

It must also be noticed considering the values reported in Table 1 that all these reactions are very exothermic. This means that a large amount of energy is made available and can locally provoke other dynamic effects damaging the substrate.

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