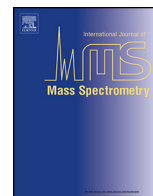




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## Modeling the intrusion of molecules into graphite: Origin and shape of the barriers<sup>☆</sup>

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### ABSTRACT

We performed density functional theory calculations to explore the energetic and geometric aspects of the permeation of  $H_2$ ,  $BeH_x$ ,  $OH_x$  ( $x = 1, 2$ ) and  $CH_y$  ( $y = 1-4$ ) through the central hexagon of coronene. Coronene serves as a cluster model for extended graphene which can be regarded as the first layer of a graphite (0001) surface. We compare the energy barriers encountered by these molecular projectiles with the ones that are obtained for atomic H, Be, C and O. The barriers are substantially lower if projectiles possess free valences that can bind to the carbon entity. Furthermore, for some of the species fragmentation is observed. Implications with respect to plasma-surface interaction are discussed.

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### 1. Introduction

Plasma-wall interactions (PWI) are the basis of plasma coating [1] and of the use of microplasmas for medical applications [2]. In thermo-nuclear research [3,4] they must be understood in terms of material degradation. PWI comprises how atoms and molecules and their ions in the plasma interact with surface materials in contact with them. Important aspects of PWI are how projectiles from the plasma or a hot gas in front of the wall can penetrate through the surface. In case of molecular projectiles, eventual fragmentation of the molecules is an issue either. The interaction of atoms and molecules with carbon materials is an especially important issue in thermo-nuclear research. Carbon fiber composites (CFC) are possibly used in the ITER (International Tokamak Experimental Reactor) device as partial coverage of the first wall [5]. There is vast experience with this material from earlier fusion experiments [6,7]. The main drawback of CFC is its high reactivity with respect to hydrogen [6]. It is expected that the latter will eventually lead to a substantial amount of tritium retained in the wall material as well as to the formation of hydrocarbon impurities polluting the fusion plasma and re-depositing at other parts of the wall [6]. The use of

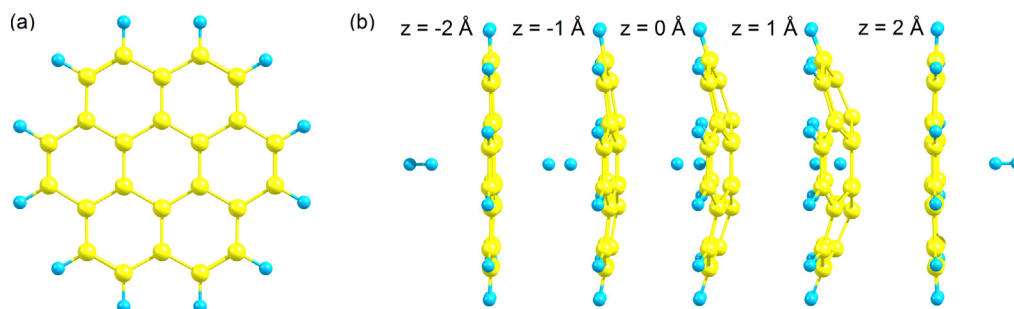
beryllium at the main wall of ITER [5] is expected to lead to the formation of beryllium hydride molecules forming another source of impurities. A rest concentration of oxygen will have the same effect leading to the formation of hydroxyl radicals and water molecules. Furthermore, recombination of hydrogen atoms leads to the formation of hydrogen molecules. Hence, the rather low temperatures of about 2–3 eV in the divertor region due to the realization of partial detachment [8,9] will give rise to a complex mixture of hydride molecules interacting with the CFC surface. For this reason, we want to explore some aspects of the interaction of such molecules with carbon sheets (as a model for the graphite structures of which CFC consists) in this work.

The interaction of molecular projectiles with fusion-relevant wall materials has been subject to a variety of experimental studies conducted in the last years [10–20]. Especially the groups of Hermann and of Märk conducted several mass-spectrometric experiments with respect to molecule/surface interactions [12,13,16–20]. They let deuterated hydrocarbon ions interact with stainless steel [10,19], carbon [11–15,17–20], beryllium [18] and tungsten [16,18]. All of these surfaces are of relevance in thermo-nuclear fusion research. The impact energies range from a few eV to hundreds of eV. Analyzed were the fragmentation processes of the incident molecules, sputtering of the material and effects due to heating of the surface. However, interpretation of experimental results is complicated due to technical difficulties such as contamination of the surfaces in course of their fabrication and unknown details of the surface structure which hinders the interpretation of the microscopic processes governing the investigated systems.

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**Fig. 1.** (a) Coronene used as cluster model for extended graphene and (b) schematic depiction of the procedure used to obtain the energy barrier for permeation of  $H_2$  through coronene. H and C atoms are depicted as light blue and yellow spheres, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

In contrast, simulations and (numerical) modeling can work on the atomistic level. Thus, PWI has also attracted a lot of interest from the theoretical side. Especially the interaction of hydrogen (and/or isotopes) with carbon-based materials has been studied extensively employing both force-field approaches [21–34] as well as quantum-chemical methods [35–43]. Also the interaction of molecules with fusion-relevant surfaces has been explored to some extent, mostly by employing force-field based simulations [28,30,34,44,45].

This study is of the quantum-chemical type. In particular, we use density functional theory (DFT) to explore the energetics of permeation of the small hydrides  $H_x$ ,  $BeH_x$ ,  $OH_x$  and  $CH_y$  with  $x = 1, 2$  and  $y = 1–4$  through the center of coronene ( $C_{24}H_{12}$ ). The latter molecule serves as a model of an extended graphene sheet. We are particularly interested in the effect of the saturation of free valences via the addition of hydrogen atoms on the energy barrier associated with the permeation process. The processes studied are far from chemical equilibrium and thus are difficult to describe quantitatively accurately. Hence, we rather aim for a qualitative exploration. Nevertheless, we will show that the trends explored indicate substantial differences in the energy barriers for atomic and molecular projectiles. This might eventually lead to a better understanding of some types of PWI.

The work is structured as follows. In Section 2, we summarize our method. In particular, in Section 2.1 we describe the cluster model used to represent the graphite (0001) surface. In Section 2.2, we describe the quantum chemical methods employed. In Section 2.3, we describe how the energy barriers are obtained and how they can be decomposed further in order to aid their interpretation. In Section 3, we discuss our results. We begin with the discussion of the differences between the energy barriers for permeation of H and  $H_2$  in Section 3.1. This is followed by analogous discussions concerning the projectiles  $BeH_x$ ,  $CH_y$  and  $OH_x$  with  $x = 0, 1, 2$  and  $y = 0–4$  in Sections 3.2–3.4, respectively. In Section 4, we discuss implications of our results in terms of conditions eventually met in future nuclear fusion applications. In Section 5, we summarize our conclusions.

## 2. Method

### 2.1. Cluster model

In order to model extended graphene sheets (serving per se as a model for a graphite (0001) surface) we use a cluster approach. In particular, we use the polycyclic aromatic hydrocarbon (PAH) coronene ( $C_{24}H_{12}$ ) as model. The molecule is depicted in Fig. 1(a). In an earlier theoretical work, it has been shown that although coronene appears rather small it is large enough to yield essential trends governing the interaction of atoms with extended graphene [43]. In this work, we adopt the strategy of this earlier investigation,

but now we move molecules rather than atoms through the center of the central hexagon of coronene. By calculating the energy at each step we determine the barrier for permeation at this site. Except for the hydrogen atoms at the edge of coronene all atomic positions are relaxed corresponding to the adiabatic interaction regime, see reference [43]. This corresponds to a velocity of the projectiles which is small enough for the carbon atoms constituting the graphite surface to adapt instantly. This appears as a reasonable assumption given the low temperature of about 2–3 eV in the divertor of a nuclear fusion scenario as envisaged for ITER. This was modeled by moving the approaching molecule along the  $C_6$  axis of coronene (the  $z$ -axis), thus performing a relaxed potential energy surface scan of the system. The  $z$ -coordinates of the coronene hydrogen atoms are fixed at  $z = 0$  and the  $z$ -coordinate of one atom of the approaching molecule is changed in steps of  $\Delta z = -0.2 \text{ \AA}$  and is also fixed while the remaining  $z$ -coordinates and all  $x$  and  $y$  coordinates of all other atoms are allowed to relax. The atoms of the approaching molecules with fixed  $z$ -coordinates have been (a) one hydrogen atom in  $H_2$ , (b) the beryllium atom in  $BeH$  and  $BeH_2$ , (c) the carbon atom in  $CH_y$  ( $y = 1–4$ ) and (d) the oxygen atom in  $OH$  and  $H_2O$ . A schematic depiction of this adiabatic permeation is shown in Fig. 1(b) for  $H_2$ .

### 2.2. DFT calculations

In order to obtain the energy profiles and intermediate geometries for permeation as described in the foregoing section we use unrestricted DFT calculations using the B3LYP [46] and PBE0 [47] functionals. Both are hybrid functionals and include a mixture of Hartree–Fock exchange and DFT exchange–correlation. The widely used B3LYP functional has been constructed semi-empirically by fitting its three parameters to experimental data. The parameter-free PBE0 functional is based on the fulfillment of a number of physical constraints. The independent and complimentary design of these functionals makes it worth to compare their results. As basis sets 6-31G [48] and 3-21G [49] have been chosen in conjunction with B3LYP and PBE0, respectively. Although they are small basis sets, it has been shown in earlier work [43] that basic trends are well preserved in them, compared with larger ones. The main reason for the choice of these functionals and basis sets is the comparability with a former work on the interaction of bare atoms with cluster models for the graphite (0001) surface [43]. To our knowledge, it has never been investigated which combination of functional and small basis set would be the best for barriers. A comparison of thermochemical data obtained from a large number of density functionals combined with small basis sets has found functionals without HF-exchange to perform best [50]. On the other side, it is known that with basis sets like 6-31G\* barriers can be calculated more accurately if more HF-exchange than 20 or 25% (PBE0 and B3LYP, respectively) is incorporated like in BH&HLYP

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