Ab initio study of the trapping of polonium on noble metals

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ABSTRACT

In the future MYRRHA reactor, lead bismuth eutectic (LBE) will be used both as coolant and as spallation target. Due to the high neutron flux a small fraction of the bismuth will transmute to radiotoxic ^{210}Po. Part of this radiotoxic element will evaporate into the gas above the coolant. Extracting it from the gas phase is necessary to ensure a safe handling of the reactor. An issue in the development of suitable filters is the lack of accurate knowledge on the chemical interaction between a candidate filter material and either elemental polonium or polonium containing molecules. Experimental work on this topic is complicated by the high radiotoxicity of polonium. Therefore, we present in this paper a first-principles study on the adsorption of polonium on noble metals as filter materials. The adsorption of monoatomic Po is considered on the candidate filter materials palladium, platinum, silver and gold. The case of the gold filter is looked upon in more detail by examining how bismuth pollution affects its capability to capture polonium and by studying the adsorption of the heavy diatomic molecules Po_2, PoBi and PoPb on this gold filter.

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The 4th generation of nuclear fission reactors will have to be inherently safer and more fuel-efficient then the nuclear power plants of today. The MYRRHA reactor, under development at SCK-CEN, will test the feasibility of 2 concepts: an accelerator driven system (ADS), and a lead bismuth cooled fast reactor [1,2]. In ADS mode, the chain of nuclear reactions can only be sustained if the combination of a proton accelerator and a spallation target feeds enough neutrons to the sub-critical core. The use of a liquid lead bismuth eutectic (LBE) both as coolant and as spallation target, will induce neutrons over a wide range of energies with little moderation, making MYRRHA a *fast* reactor. This will allow to transform the more abundant ^{238}U (abundancy 99.3%) into ^{239}Pu which can be burned, rather than using only a limited fraction of natural uranium directly, i.e. ^{235}U (0.7%), as done in most present nuclear power reactors [3].

An issue with this type of reactors is the production of polonium as result of the transmutation of mainly bismuth. During the operation of MYRRHA, a non-negligible amount of polonium will be present in the LBE coolant. Part of the polonium will evaporate to the cover gas above the liquid LBE. Polonium has no stable isotopes. Its longest-lived isotopes, ^{210}Po (138.3 days), ^{208}Po (2.90 years) and ^{209}Po (102 years) are all strong α-emitters. Because of the relatively short half-lives, polonium isotopes are strongly radioactive, e.g. 1 mg ^{210}Po has an activity of 166.25 GBq, while 1 mg of ^{208}Po reaches 21.74 GBq. As a result, polonium is highly radiotoxic upon inhalation. This makes it cumbersome to study, for instance, the thermodynamic properties of macroscopic quantities of polonium-containing molecules and solids experimentally [4,5].

In order to prevent a build-up of polonium and other malicious elements in the gas phase, the atmosphere inside MYRRHA's closed reactor vessel will be continuously filtered [1,6,7]. Developing appropriate filter systems requires an adequate knowledge of polonium chemistry. Exactly this is the bottleneck: due to the aforementioned difficulties the experimental information that is available in the literature is insufficient. Even worse: as most experimental studies date back to the 60's of the past century and

earlier [8,9,5], merely reproducing them today is not easy with modern safety restrictions. In recent years, within the framework of ADS systems, much effort has been put into a better understanding of polonium and its interaction with LBE and different atmospheres: evaporation [10–13] or extraction [14,15] from LBE and the volatility of polonium molecules [16,4]. Also the use of transition metals and noble metals as filter materials is a subject of study [17]. Around 1980 a few studies on the adsorption and desorption of polonium from the gas phase on noble metals were performed by Gäggeler et al. [18,19].

Polonium, being experimentally hard to access, is an ideal example of a research topic where modern first principles methods can play a role. Available computational studies on polonium focus on its peculiar simple cubic ground state structure [20–22], on its role in the homologous series connecting selenium and tellurium with livermorium [23,24], or on it being a constituent of hypothetical semiconductors [25]. In all these cases, the relevance lies in a more fundamental understanding, rather than in practically useful polonium chemistry. A first computational effort into the latter direction has been delivered by Ayala et al. [26] in 2008 by studying the hydration of Po(IV) in solution. Rijpstra et al. [27] focusses on the interaction between polonium and LBE in the solid state. More recently the formation of several polonium-containing molecules, whose existence is expected in a LBE environment, has been studied in Van Yperen-De Deyne et al. [28]. In the present work we use density functional theory (DFT) to examine the interaction between a low concentration of monoatomic polonium and the surfaces of the candidate filter materials palladium, silver, platinum and gold. For the case of a gold filter, we investigate the adsorption of the diatomic molecules Po_2, PoPb and PoBi and the effect of bismuth pollution.

1. Methods

1.1. Computational settings

All calculations in this work are performed within density functional theory (DFT) [29,30] as implemented in the 'Vienna ab initio simulation package' (VASP) [31]. The projector augmented wave (PAW) method [32,33] is used to solve the scalar-relativistic Kohn−Sham equations. The exchange-correlation energy is described by the Perdew-Burke-Ernzerhof (PBE) functional [34]. VASP incorporates by default scalar relativistic effects [35]. Since we are dealing with mainly heavy elements, the next order of relativistic effects, spin−orbit coupling (SO), is taken into account selfconsistently [36,37].

VASP is a periodic code in which all observable properties of a crystal can be expressed as integrals over the unit cell (first Brillouin zone) of the reciprocal space. Through the Bloch theorem [38], the wavefunction for every point in reciprocal space is represented by a Fourier series of plane waves. Two parameters determine most of the computational precision. One of these is the k-point grid that is used to sample the integral over the first Brillouin zone. The second parameter is the energy of the last plane wave in the Fourier series, the so-called cut-off energy. In order to find a good balance between computational precision and computational cost, we computed for face centred cubic (fcc) gold and fcc palladium the energy difference between the ground state volume and a 5% expanded volume, for a wide range of both k-grid densities and cut-off energies. We concluded that Γ-centred Monkhorst-Pack k-grids [39] with a density of 216000 k-points/Å^{-3} and a cut-off energy of 330 eV were sufficient to obtain a numerical accuracy for energy differences better than 0.001 eV/atom for gold and 0.002 eV/atom for palladium. For the molecular adsorption calculations a cut-off energy of 550 eV was used, leading to even smaller errors. Fermi level smearing of 0.01 eV (bulk calculations) or 0.1 eV (surface calculations) was used with the first order Methfessel-Paxton method [40]. During geometry optimization, we considered a structure converged when all forces on the atoms are below 0.01 eV/Å, unless the atoms were kept fixed within the cell.

One of the quantities required to determine the adsorption enthalpy is the energy E_u of the free adsorbent u (see Eq. (1) later on in Section 1.3.1). Preferentially, these calculations should be performed within the same periodic code as applied for the slab on which u will be adsorbed. Sufficiently large unit cell sizes should be taken into consideration to avoid interaction with periodic images of u. While we use cells of 15 Å × 15 Å × 15 Å for the monoatomic energies, for the diatomic molecules we consider unit cells of dimension 15 Å × 15 Å × 18 Å, with the largest size in the direction of the internuclear axis of the molecule. The energies obtained for molecules in these large empty unit cells should be comparable with non-periodic calculations, obtained in a non-periodic code using the same DFT functional.

1.2. Level of theory

In order to assess the level of theory that will be required, we compare in Fig. 1 formation enthalpies for Po_2, PoPb and PoBi (the formation enthalpy ΔH_{form} is the difference between the free molecule enthalpy E_u and the sum of the free atom enthalpies). These formation enthalpies are computed by three different methods: at one hand a high level method − Multi-Reference Configuration Interaction (MRCI) by the non-periodic ORCA code, and at the other hand either the regular PBE functional or the more expensive hybrid PBE0 functional, both by the periodic VASP code. The influence of inclusion of exact Fock exchange is examined by comparing a pure functional (PBE) and a hybrid functional (PBE0).

In Ref. [28], it was already shown that PBE0 succeeds surprisingly well in reproducing the formation energies obtained by the much more accurate MRCI method, within 0.2 eV. From Fig. 1a and b, it can be seen that the PBE functional follows the PBE0 results closely. When calculating a linear regression for all PBE values obtained with VASP against those obtained for PBE0, both with and without SO and including the hypothetical solid PoAu as an additional case, we find $\Delta H_{form}(PBE) = 1.09 \Delta H_{form}(PBE0) - 0.17$ eV/u with a standard error on the PBE values of 0.10 eV/u. Considering these small differences, and considering the fact that adsorption calculations are intrinsically much more time-consuming than free molecule calculations, we conclude that it is justified to perform the adsorption calculations with the less expensive PBE functional.

Whereas MRCI and PBE/PBE0 are in fair agreement with each other when no spin−orbit interaction is included (Fig. 1a), this agreement vanishes upon adding spin−orbit coupling (Fig. 1b). In the latter case, there is very little spread in the DFT results, while for MRCI a much larger difference between the three molecules is found. This can be understood when considering the interplay of symmetry and degeneracy: a diatomic molecule has a high symmetry, which leads to degeneracy of several molecular orbitals. When such degeneracies are present, a high-level multireference method as MRCI leads to results that are different from what is obtained by regular single-reference DFT, with the former being the more accurate one. In the absence of degeneracies − as happens for low-symmetry cases − both methodologies lead to much more similar results. The case of a molecule on a surface has a reduced symmetry, and therefore the deviation by PBE/PBE0 is expected to be much smaller for adsorption energies. Another feature that contributes to the deviation in Fig. 1b is the fact that spin−orbit coupling is treated in different ways in both codes: perturbatively in ORCA (MRCI) and self-consistently in VASP (PBE/PBE0). The latter is more correct. Concerning the differences between the GGA (PBE)