Trapping of volatile fission products by C_{60}

Navaratnarajah Kuganathan [a, *], Ashok K. Arya [b], Michael J.D. Rushton [a, c], Robin W. Grimes [a]

[a] Department of Materials, Imperial College London, London, SW7 2AZ, UK
[b] Material Science Division, Bhabha Atomic Research Centre, Trombay, Mumbai, 400 085, India
[c] College of Physical and Applied Sciences, Bangor University, Bangor, Gwynedd, LL57, UK

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Carbon based filters provide important safety barriers that remove volatile fission products from gas streams. The capacity and efficiency of a filter to trap fission products depends upon the strength of the interaction between the fission products and the filter material. In this study, we apply density functional theory together with a dispersion correction (DFT + D) to predict structures and energies of volatile fission product atoms and molecules trapped by buckminsterfullerene (C_{60}). Endohedral encapsulation energies and exohedral association energies show that Rb and Cs are strongly trapped as ions, each transferring approximately one electron to C_{60}. Kr and Xe are weakly trapped atoms with Xe showing a preference for exohedral association and Kr for endohedral encapsulation. Br, I and Te, while strongly trapped from atoms (and assuming charge from C_{60}) are thermodynamically more stable as neutral covalently bonded Br_2, I_2 and Te_2 molecules weakly trapped through van der Waals forces, exohedrally. Heteronuclear CsBr and CsI were also considered. Both molecules were non-bonded to C_{60} with similar association energies to those exhibited by Br_2, I_2 and Te_2.

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1. Introduction

Gaseous effluents, generated during processing of spent fuel, contain radioactive volatile species including alkali metals, halogens and noble gases [1]. Among these, species such as iodine and strontium can be concentrated by the body, increasing the radiotoxic impact [2]. To minimize the hazard, radioactive species should be removed through either physical or chemical capture before the effluent is discharged to the atmosphere. Filters, in particular activated carbon filters, are mostly used to remove gaseous iodine species [3]. However, other porous materials including zeolites, silica, alumina and metal organic frameworks have been studied experimentally to improve the effectiveness of filters [3,4]. The search for alternative filter media that can trap volatile gases continues. Such materials must be thermodynamically stable, chemically active, have adequate mechanical properties and a high surface area, whilst still being manufacturable at scale in a cost-effective manner.

The buckyball structured carbon fullerenes and fullerites are

candidate materials for trapping volatile fission products (FP). They provide both inner and outer surface structures, high resistance to external chemical attack, are light weight and exhibit mechanical stability at high pressure and temperatures [5]. Buckminsterfullerene (C_{60}), consists of 60 carbon atoms and has been widely studied [6]. The interior and exterior of a C_{60} molecule are surrounded by an electron charge density of conjugate π bonds each formed between two adjacent carbon atoms. The charge density of the inner space is therefore higher than the outer surface. The encapsulation of species within C_{60} has been described in various experimental and theoretical studies: alkali metals (e.g. Li, K) [7,8], alkali earth metals (e.g. Ca, Sr and Ba) [7,8], radioactive isotopes (e.g. ^{159}Gd, ^{161}Tb) [9,10], actinide metals (e.g. Lr) [11], non-metals (e.g. N, P) [12,13], noble gases (e.g. Ne, Ar) [14,15], transition metals (e.g. Tc, Fe) [16,17] and rare earth metals (e.g. La) [18]. These have all been considered either in the form of atoms or clusters. The external surface of C_{60} has been studied theoretically for its interaction with transition metal atoms and clusters, and shown to provide a good catalyst for the activation of di-nitrogen molecules [19] and the storage of hydrogen [20]. Furthermore, the theoretical study by Ozdamar et al. [21] demonstrated the stability and electronic properties of Pt and Pd in the form of atoms and dimers interacting with the outer surface of C_{60}. Likewise, hydrogen absorption has

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* Corresponding author.
E-mail address: n.kuganathan@imperial.ac.uk (N. Kuganathan).

been considered on the surface of Pd-decorated C_{60} by El Mahdy [22]. Thus, C_{60} provides different sites to capture species both internally (endohedral) and externally (exohedral).

This study uses density functional theory (DFT) together with dispersion corrections, to investigate the thermodynamical stability of gaseous volatile fission products (Kr, Xe, Br, I, Rb, Cs and Te) in order to understand whether they can be trapped by filters that incorporate C_{60}. For those species that may become bound to C_{60}, calculations have been performed to establish whether there is a preference for positions inside or on the surface of the fullerene cages and whether they become bound as atoms or in the form of dimers. DFT calculations, in addition to giving structural information, provide data on electronic properties, which are also discussed.

2. Computational methods

Calculations were carried out using the spin-polarized mode of DFT as implemented in the VASP [23,24] package. The exchange-correlation term was modelled using the generalized gradient approximation (GGA) parameterized by Perdew, Burke, and Ernzerhof (PBE) [25]. In all cases, we have used a plane-wave basis set with a cut-off value of 500 eV. Structural optimisations were performed using a conjugate gradient algorithm [26] and the forces on the atoms were obtained via the Hellman-Feynmann theorem including Pulay corrections. In all optimized structures, forces on the atoms were smaller than 0.001 eV/Å and all the values in the atomic stress tensor were less than 0.002 GPa. All calculations were performed without using symmetry restrictions. All geometry optimisations were performed using a single k-point. To calculate the density of states (DOS), a $4 \times 4 \times 4$ Monkhorst-Pack [27] k point mesh, which contains 36 k points was employed. A cubic super cell with a length of 25 Å was used for all configurations to ensure that adjacent structures do not interact (the largest linear dimension of a C_{60} molecule was 7.10 Å). We define encapsulation energy (for singe atom or dimer trapping inside the cage) and association energy (for single atom or dimer trapping outside the cage) by the following equation:

$$E_{Enc/Assoc} = E\,(FP\text{-}C_{60})\,-E\,(C_{60})\,-n\,E\,(FP) \qquad (1)$$

where $E\,(C_{60})$ is the total energy for the isolated C_{60} molecule, $E\,(FP\text{-}C_{60})$ is the total energy of the gaseous atom or atoms occupying the centre of the C_{60} cage or interacting on the surface of C_{60}, $E\,(FP)$ is the total energy of an isolated fission product (the reference state) and n is the number of fission product atoms considered in the process.

The inclusion of van der Waals (vdW) forces are particularly important for the interactions of the highly polarizable noble gases and transition metal atoms with C_{60}. Here, dispersion has been included by using the pair-wise force field as implemented by Grimme et al. [28] in the VASP package.

3. Results and discussion

3.1. Structural and electronic properties of C_{60} fullerene molecule

A C_{60} fullerene molecule is spherical with truncated icosahedral (I_h) symmetry. It consists of 12 pentagonal rings, 20 hexagonal rings and 32 faces as shown in Fig. 1a. There are two distinct alternate C–C and C=C bonds present in the molecule with the experimental bond lengths of 1.43 Å and 1.39 Å respectively [29]. In order to validate the computational parameters used in this study, we carried out an energy minimisation calculation to optimize the structure of a C_{60} molecule. In the relaxed structure, we calculated
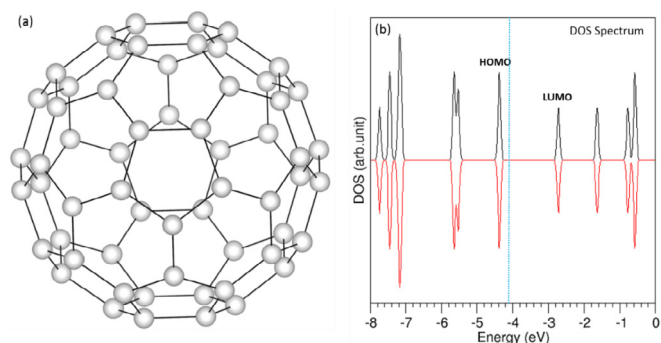
Fig. 1. (a) Optimised structure of a C_{60} molecule and (b) its density of state spectra. The vertical dotted line, at ~ −4.10 eV, corresponds to the Fermi energy. (A colour version of this figure can be viewed online.)

the equilibrium bond distances, energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) and the net magnetic moment, to compare with experimental and other theoretical values.

The calculated bond lengths of C–C and C=C were 1.45 Å and 1.40 Å respectively, which agree well with experimental values [29] and other theoretical calculations [22]. The calculated HOMO-LUMO gap of the C_{60} molecule is 1.55 eV, in good agreement with the value of 1.64 eV calculated by the DFT calculations of Goclon et al. [30]. Our calculation shows that the C_{60} molecule is non-magnetic (see Fig. 1b) as predicted in previous studies [31].

3.2. Initial configurations

We considered six different sites for the absorption of fission products (FP). In the first configuration, the FP occupies the center of the cage [endohedral C_{60} (**E**)], as shown in Fig. 2 (a). In terms of surface sites, there are five possible initial positions as shown in Fig. 2 (b) − (f). These are: (b) on top of the center hexagonal ring (**H**), (c) on top of the center pentagonal ring (**P**), (d) on top of a C-C bond between two hexagonal rings (**66**), (e) on top of a C-C bond between an hexagonal ring and a pentagonal ring (**65**) and (f) on top of a C atom on the C_{60} cage (**C**).

3.3. Formation of single gaseous fission products interacting with C_{60}

First we consider the stability of the fission products (Xe, Kr, Br, I, Cs, Rb and Te) as single atoms occupying the centre of the C_{60} cage. In relaxed configurations, the positions of the fission product atoms remain very close to the centre of the cage. The encapsulation energy for the fission products within the C_{60} cage depends on the relative ionization potentials and electron affinities of the atom and the C_{60} molecule but also the size of the atom or ion relative to the size of the internal volume of C_{60}. Fig. 3 (a) shows the calculated ionization potentials and the electron affinities of the fission product atoms and C_{60} together with values reported in the data book [32]. Though the trend agrees well with the values reported in the data book, the current DFT calculations underestimate the first ionization potentials and overestimate the electron affinities. This is because of the ionization energies and electron affinities calculated from DFT orbital energies are usually poorer than those of Koopmans' theorem, depending on the exchange-correlation approximation employed [33,34].

Both Rb and Cs have lower ionization potentials and lower electron affinities than the C_{60} molecule. A lower ionization potential enables the (easy) removal of the outermost electron from