Chemical Modeling of the Capture of Radioiodine Species

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1.0 Introduction

Iodine is a common fission product resulting from the transmutation of uranium fuel in nuclear power reactors. The short-lived radioactive isotope, ^{131}I, with a half-life of around eight days, would be a particular health concern if released into the environment. Capture materials, such as activated carbon, are used routinely in nuclear power plants[1,2] and medical isotope production facilities[3] to remove this hazard during normal operations to reduce emissions to acceptable levels. Iodine, unlike other common fission products such as noble gases, is challenging because of the wide range of molecular forms and oxidation states (from +VII in IF_7 to -I in iodide) that it displays, which can interconvert both in the gas phase and in the solution phase for example. In the atmosphere, a variety of chemical forms are observed due to radical pathways that can be initiated by interaction with light, whereas in the solution phase, iodide (I^-), iodate (IO_3^-) and molecular iodine (I_2) are the most common species. In the event of a nuclear incident and subsequent release of radioactive iodine, such as the Fukushima accident, iodine-containing species could potentially interact with a number of surfaces causing further molecular interconversions, including the stainless steel reactor vessel, soil in the sub-surface and particulates in the atmosphere. Consequently, a detailed understanding of these complex chemical networks is required to design effective emergency response to contain the hazard to human health. The foundational science needed as a basis for this understanding begins with simple models of how iodine-containing molecules interact with surfaces such as pristine graphite surfaces as surrogates for one of the most important components in an activated carbon material.

The work in this project is focused on three computational tasks. In the first, we consider the binding of iodine-containing molecules of varying oxidation states to the major component of activated carbon – pristine graphene-like sheets. The aim of this task was to verify that the main mode of interaction with the surface was through physisorption. The second task focused on molecular binding and possible chemical transformations resulting from the reaction of molecular iodine with chemical functional groups on the edge of the graphene sheets or surface defects in the sheet itself. Spectroscopy and elemental analysis has shown the presence of a small number of these groups and adsorption measurements indicate these sites may lead to irreversible adsorption of iodine likely from a chemisorption process. The exact nature of these effects at the atomic level is not known and this task was focused on investigating these processes. The final task was associated with radiolytic breakdown of ^{131}I to [131]Xe in iodine-containing molecules and investigated the resulting molecular fragmentation process both in the gas phase and on the graphene-like surface. For each of the tasks, the intent was to learn about the thermodynamics and kinetics of the chemical transformations and use the calculations to provide parameters for input into kinetic models describing these processes for interpretation of experimental data in future work.

2.0 Binding of Iodine-Containing Molecules to Graphene Sheets

2.1 Background

This task is focused on calculations of the binding of iodine-containing molecules to graphene surface models. To increase the sophistication of the models, we consider several layers of graphene in the model so that the sub-surface effects that would be present in graphite are included.

The interaction of iodine-containing species with carbon-based capture materials has been studied extensively both experimentally and theoretically with a focus on molecular iodine, I_2. Measurements have been made to probe the adsorption and desorption behaviour on activated carbons[4–8] and also other carbon materials such as graphite,[9,10] coal[11] and carbon black.[12] Notably, Park and Yang[8] determined the activation energy for desorption to be approximately 51 kJmol^{-1}, which is a direct measure of the strength of interaction between iodine and the sorbent. Salzano measured both physisorption and chemisorption during adsorption of iodine on graphite.[9] Iwamoto and Oiski showed that both the heats of adsorption and activation energies for desorption varied with coverage for iodine on graphite.[10] The heat of adsorption were reported as ranging from 50-79 kJmol^{-1}, whereas for the activation energy of desorption distinction was made between physisorbed iodine (79-130 kJmol^{-1}) and chemisorbed iodine (142-200 kJmol^{-1}). Kipling and co-workers make conclusions regarding the packing structure of molecular iodine on the carbon surface based on the measured adsorption capacity,[12] and related it to that observed in the molecular iodine crystal structure. Although direct structural observation of iodine on the carbon surface are difficult, spectroscopic probes can provide useful information. Ghosh and co-workers performed measurement of shifts in Raman bands on adsorption of halogen molecules on nanotubes and graphene, and correlated the observations with density functional theory calculations.[13] They observed a relationship between the electronic structure perturbations and the electron affinities of the molecules.

The majority of the computational studies have focused on the behavior of molecular iodine bound to graphene surfaces. Gerber and co-workers studied the adsorption of both atomic and molecular iodine on graphene surfaces using a number of a density functionals including non-local van der Waals corrections.[14] The calculated adsorption energy is strongly dependent on the binding site geometry and spans a range of 30-50 kJmol^{-1}. Rudenko and co-workers investigated the binding of diatomic halogen molecules to graphene surfaces using a van der Waals density functional methods.[15] They calculated binding energies ranging from 34-36 kJmol^{-1} for out-of-plane geometries and 48-50 kJmol^{-1} for in-plane geometries. They also predict the contribution of charge-transfer to the binding energy.

In this task, we present a comprehensive fundamental computational study addressing the interaction of a number of iodine-containing molecules with a graphite surface examining the effect of choice of modelling approach, system size and model representation to predict binding geometries and energetics. In particular, we probe the extent to which charge transfer may occur between the surface and the sorbed molecule to understand the balance between physisorption and chemisorption effects.

2.2 Methods and Models

The graphite (0001) surface was employed as a surrogate model for the surface of activated carbon. The slab is shown in Figure 1. The exposed surface is a plane of sp^2 hybridized carbons corresponding to a single graphene layer. The slab model contains three layers with the middle layer offset from the top and bottom layers. This arises from the crystal structure of graphite, and it means that the central layer has carbons lying below the hexagon centers (hollow sites) and half of the carbon atom in the surface layers. Adopting an odd number of layers allows for the top and bottom layers to be aligned.

Figure 1: Structural models used in this study. These are a) the 4-atom hexagonal unit cell of graphite, b) the 3x3 hexagonal slab (54 atoms), c) the 5x5 hexagonal slab (150 atoms), and d) the orthorhombic slab (216 atoms). Brown and silver balls represent carbon atoms, but the silver coloured atoms in the slabs are in the subsurface layer.
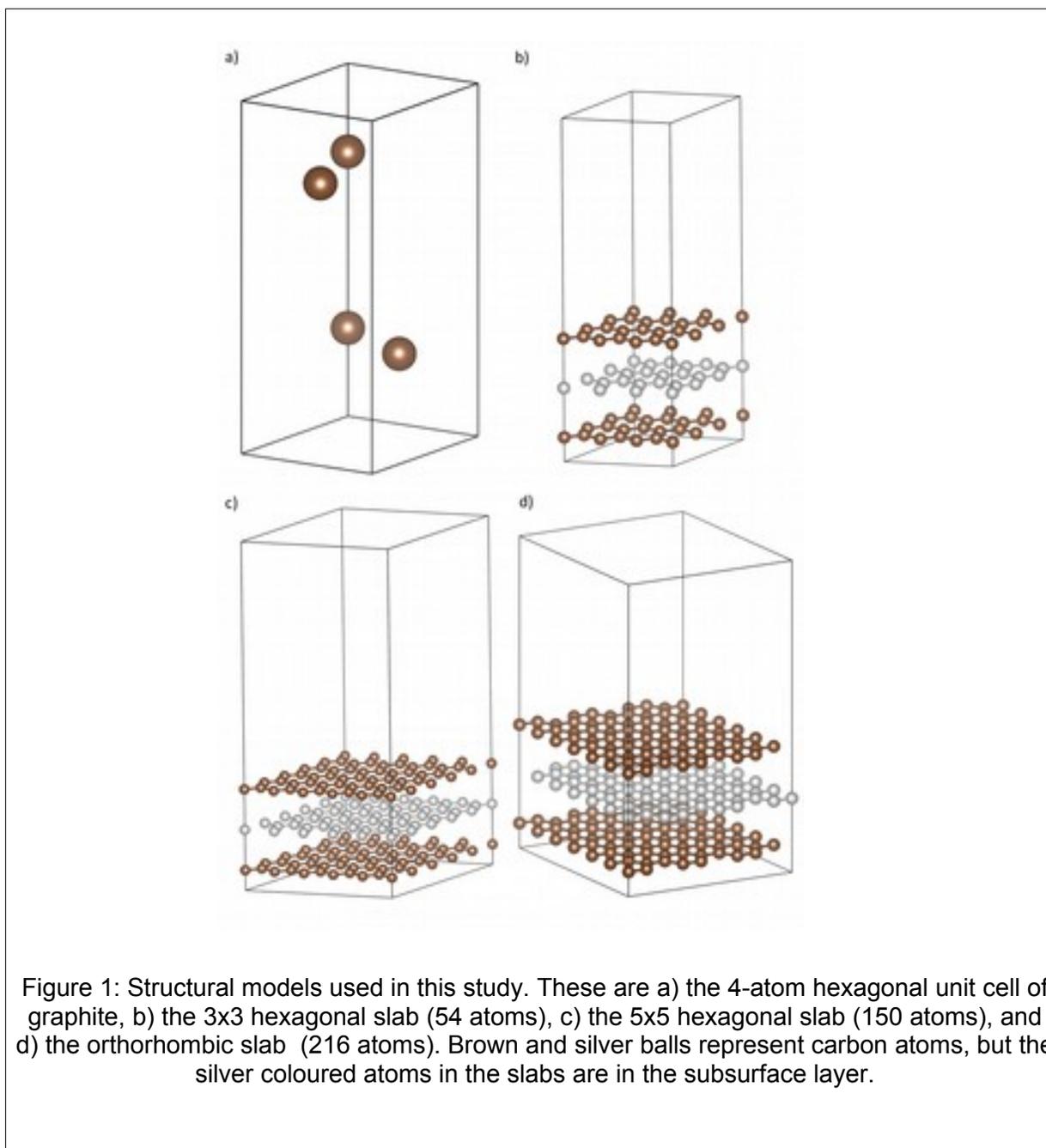
Spin-polarized Kohn-Sham density functional theory (KS-DFT)[16,17] calculations were performed using the Vienna *ab Initio* Simulation Package (VASP) version 5.4.4.[18–20]   The projected augmented-wave method (PAW) was used to represent the interactions between nuclei and electrons.[21] Standard (not soft) PAW potentials were taken from the VASP library[22] with the following valence electrons treated explicitly: H $(1s^1)$,C $(2s^22p^2)$, O $(2s^22p^4)$, and I $(5s^25p^5)$. Electron exchange-and-correlation (XC) was treated within the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof[23] (PBE) and the strongly constrained and appropriately normed (SCAN)[24] meta-GGA functionals. The plane-wave kinetic energy cutoff was 900 eV. For the hexagonal graphite unit cell, a 15 x 15 x 9 γ-centered mesh was used, and super-cell calculations were adjusted to keep the k-point spacing approximately constant. Gaussian smearing with a width of 0.1 eV was employed. This approach keeps the entropic contribution to the total energy below 1 meV/atom. With these parameters, the total energy of the graphite unit cell (4 atoms) was converged to 1 meV/atom. Bulk system band structures were computed using the improved tetrahedron method of Blőchl, Jepsen, and Andersen.[25] For slab calculations, only 1 k-point was used in the direction normal to the surface to minimize interactions between the slab and its periodic image. At least 10Å of vacuum was placed between the slab and its periodic image.

Graphite contains carbon atoms covalently bonded in planes. The layers are held together through dispersion (van der Waals) interactions. GGA functionals such as PBE poorly describe dispersion as evidenced by the lack of adhesion between layers in graphite. It is expected that meta-GGA functionals should incorporate some intermediate-range dispersion interactions.[26] However, several methods have been proposed to correct for this behavior. These fall into two classes: *a posteriori* corrections that depend on an empirical potential (for example, Grimme's DFT-D family of corrections)[27] and self-consistent corrections where an explicit dispersion term is added to the XC functional (for example, the DFT-DF approach).[28] In this work, we employ Grimme's DFT-D3 approach to dispersion interaction.

2.3   Results

Figure 2: The two most favorable I_2 adsorption configurations on graphite: (a) hollow-hollow configuration, and (b) the offset configuration
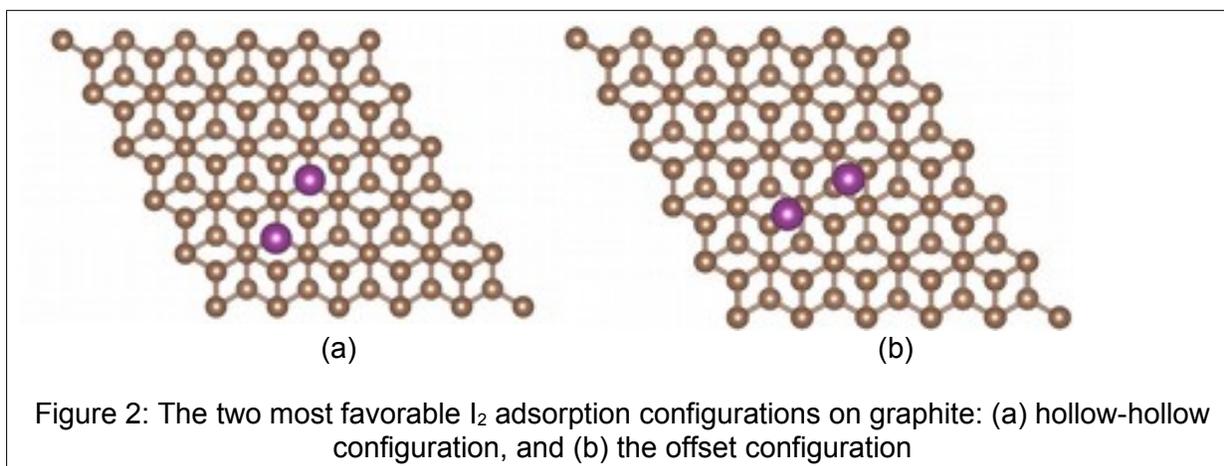
The analysis of I_2 adsorption on graphite requires considering the structure of the graphite (0001) surface. The 3x3 surface slab was used for an initial survey of the potential sites where molecular iodine could adsorb. High-symmetry sites were used to anchor the first iodine atom, and the second was placed either directly above the first atom or over another high symmetry

site with the I_2 molecule angled upward from the first atom to the second atom. This initial geometry search revealed that the most favorable conformation was placing the I_2 parallel to the surface. Furthermore, two configurations had the strongest adsorption energies (Figure 2). The first configuration involves the iodine atoms each sitting above a hollow site. The second configuration has one iodine displaced from the hollow site toward a top site while the second iodine resides on (or near) a bridge site. The adsorption energies computed with the PBE-D3 methodology are 33.1 and 32.4 kJ/mol, respectively. Pure PBE calculations for the hollow-hollow configuration give a binding energy of less than 1 kJ/mol. This indicates that surface-I_2 interaction is almost all dispersive.

The simplest non-diatomic molecule containing iodine is hypoiodous acid, HOI. This species is frequently discussed in the context of molecular iodine dissolving into aqueous solutions.[29] However, it is a likely species in a nuclear reactor effluent.[1] The HOI molecule is bent which adds numerous adsorption configurations. Namely, does the molecule lie flat, or at an perpendicular to the surface? What atom prefers to be closest to the surface, and where is the molecule positioned relative carbons in the surface layer?

To answer these questions, we start with three possible configurations of the HOI molecule featuring the I-O bond parallel to the surface and the O-H bond directing the H atom toward the surface (down), parallel to the surface (flat), or away from the surface (up) as shown in Figure 3. These configurations are augmented by placing the iodine above the high-symmetry sites (hollow, top, bridge) and rotating the molecule such that the I-O bond is directed toward an adjacent high symmetry site though the O will not lie directly on top of that site. Optimization of the initial configurations using the PBE-D3 approach reveals that the flat configuration is not stable and results in the hydrogen rotating into the down configuration.

(a)   (b)   (c)

Figure 3: Calculated HOI adsorption sites: (a) H-up, (b) H-down, and (c) H-horizontal
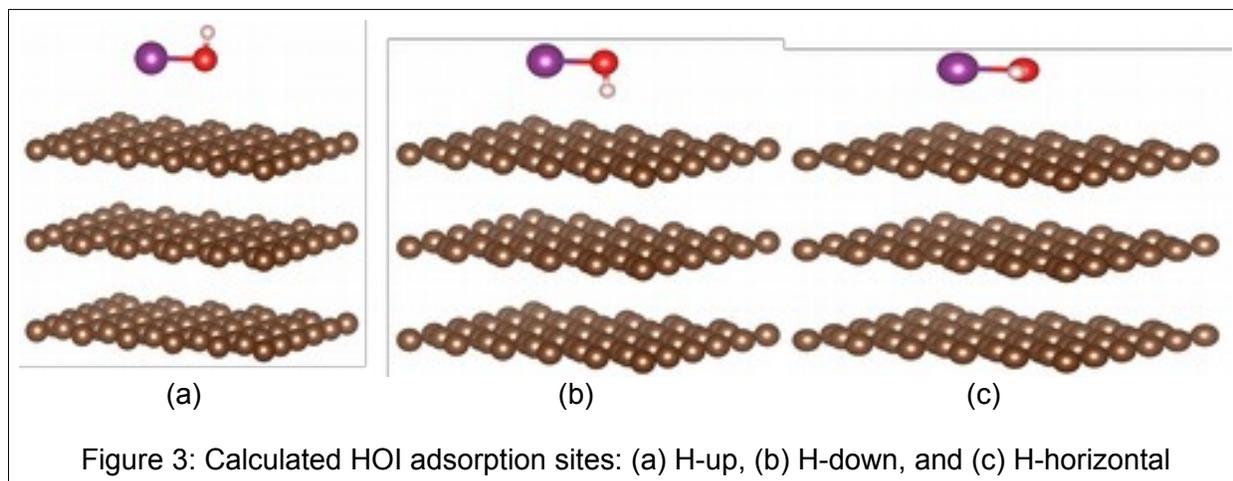
After optimization, the strongest adsorption occurs with the iodine on a hollow site and the oxygen sitting on a bridge site with the I-O bond crossing a top site. The hydrogen is pointing down. Ultimately, adsorption in this configuration is favorable by 30.8 kJ/mol. The complete set of adsorption results shows that the iodine prefers the hollow site by approximately 6 kJ/mol and that having the hydrogen point toward the surface is preferable by 5-6 kJ/mol. The surface-iodine distance is comparable to the adsorption of I_2 *vide supra* which leaves plenty of space for the oxygen and the hydrogen to move toward the surface. This adds favorable dispersion interactions with the surface resulting in a lower adsorption energy. The most favorable configuration suggests that monolayer adsorption of HOI would involve one molecule per hollow site.

A Bader charge analysis of the HOI molecule shows that no charge transfer occurs upon adsorption. This is not unexpected, however, since the electron density arises from a DFT-PBE calculation which fails to property describe dispersion interactions. Thus, no significant perturbation happens to the HOI molecule when it adsorbs to the surface.

3.0 Binding of molecular iodine to edge sites

3.1 Background

Activated carbon (AC) is a sorbent material that has been utilized in capturing radioactive contaminants, including [131]I. However, the mechanisms for AC's capture of iodine are not well understood— for example, AC has edge groups and chemistry that can vary depending on its source[30] and the treatments it has undergone.[31–35] It is also unknown to what extent iodine may be chemisorbed (adsorbed via chemical reactions) vs. physisorbed when captured by AC. However, if chemisorption is to occur, it will most likely happen near functional groups at AC edges which are chiefly responsible for AC's surface chemistry.[31] We used first principles calculations to predict whether chemisorption of iodine is energetically favorable at common AC edge sites. It is unfeasible to represent the complex structure of AC at this scale, so we use graphene nanoribbons and flakes as surrogates for AC, as shown in Figure 4. Oxygen is the main non-carbon species present in AC, and is responsible for much of its chemistry,[31] so we focus on simple functional groups that contain oxygen, including phenol and carboxyl groups.

3.2 Methods and Models

To model graphene nanoribbons we performed DFT calculations using VASP ,[18,20,36] while *ab initio* calculations were implemented for graphene flakes using NWChem.[37] We quantified the energetic favorability of iodine chemisorption at an edge site by computing the reaction energy (heat of formation) by the simple equation

$\Delta E_{reaction} = \sum E_{products} - \sum E_{reactants}$,

where a negative value indicates that the reaction is favorable (exothermic), and a positive value indicates the reaction is unfavorable (endothermic).
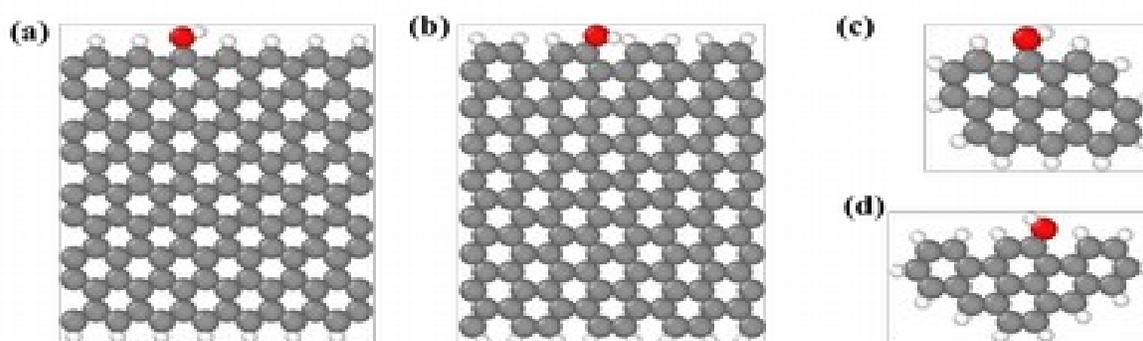
Figure 4: Surrogates for activated carbon (AC) edges, with phenol functional group shown as an example. AC is represented by either graphene nanoribbons (a-b), or graphene flakes (c-d), with either zigzag (a, c) or armchair (b, d) edges.

3.3 Results

The chemisorption reaction energies of the iodine species I_2 and HI at pristine edges and at phenol edge groups are listed in Table 1. Results from NWChem and VASP were in reasonably good agreement despite the difference in their structure (flake and nanoribbon respectively). We found that zigzag edges tended to be more energetically favorable than armchair edges. However, in all cases we found iodine chemisorption to be highly endothermic and therefore unfavorable. This is especially true when oxygen is present. The other edge groups we tested yielded similar results, indicating that chemisorption is unlikely to occur at either pristine edges or at oxygen-based functional group sites. This is surprising as there is evidence that iodine chemisorption into activated carbon can and does occur. We are currently investigating different routes to chemisorption, including through epoxide groups which are present in graphene oxide and that may facilitate iodine chemisorption, or via other elements such as potassium that may serve as catalysts.

Table 1: Predicted reaction energies for chemisorption of iodine species on pristine edge or phenol edge group. Graphene flake images are shown in the table to represent the given reaction, but note that VASP calculations use nanoribbons as shown in Figure 1(a-b). Carbon atoms are grey, hydrogen atoms are white, oxygen atoms are red, and iodine atoms are purple.

4.0 Transmutation of radioiodine containing molecules

4.1 Background

I_2 and CH_3I can be generated in the upper ocean layers and migrate the atmosphere.[38] Photolysis and ozonolysis reactions convert these species into iodine oxides (IO_x) and acidic iodine (HIO_x) species,[39–41] generating a wide array of iodine-containing chemical species in the atmosphere with a large number of oxidation states possible, ranging from –I to +V. In the case of radioiodine, this complex iodine chemistry is further complicated by the short a half-life of ^{131}I, about 8 days,[42] after which it undergoes β-decay leading to the creation of ^{131}Xe and the emission of an anti-neutrino ($\acute{v}_e$), a β⁻ particle, and γ-rays:

$$^{131}_{53}\text{I} \longrightarrow \beta + \bar{v}_e + {}^{131}_{54}\text{Xe}^* + 606\,\text{keV}$$

$$^{131}_{54}\text{Xe}^* \longrightarrow {}^{131}_{54}\text{Xe} + \gamma + 364\,\text{keV}$$
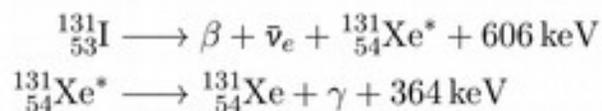
Upon decay, ^{131}I releases a total of 970 keV of energy in a two-step process. The first step involves the emission of β-particles having a maximum kinetic energy of 806.9 keV, followed by the emission of γ-rays with a most probable energy of 364 keV. At the end of the decay process, a stable daughter ^{131}Xe isotope is created. While the β-particles can travel up to 0.2 cm away in water[43] from the ^{131}Xe nucleus, the physical and chemical changes induced by the transmuted ^{131}Xe have effects on the nanometer scale. In a molecular context, the local perturbations imposed by ^{131}I transmutation at first seem insurmountable as four different atomic-scale disruptions arise: (i) the abrupt appearance of a xenon nucleus, (ii) the creation of a positively charged Xe ion isoelectronic with its parent, (iii) potential additional ionizations due to the reorganization of the electron cloud adjusting from ^{131}I to $^{131}Xe^+$ nucleus (a process also referred as electron shake-off[44]), and (iv) a physical recoil of the daughter Xe nucleus, in which a certain amount of kinetic energy is given to Xe in accordance with momentum conservation between the energy released during radioactive decay and the products of the reaction. Altogether, these effects have the potential to break bonds and create new chemical environments which could potentially alter the properties of capture materials.

4.2 Methods and Models

The Vienna *ab Initio* Simulation Package (VASP) package[13] has been used to perform AIMD modeling of bond breaking events in molecules after ^{131}I transmutation. The generalized gradient approximation (GGA) exchange-correlation functional, as parametrized by Perdew-Burke-Ernzerhof,[14] with the Grimme[15] dispersion corrections (i.e., PBE+D3) has been used in all the simulations. The PAW potentials for H, C, O, I, and Xe respectively used a valence electronic configuration of $1s^1$, $2s^2\,2p^2$, $2s^2\,2p^4$, $5s^2\,5p^5$, and $5s^2\,5p^6$. The simulations were performed in the NVE ensemble with a 0.1 fs time step and an electronic self-consistent field energy convergence criterion of 10^{-6} eV/cell. To correctly describe bond breaking events, spin-

polarization was used. Bond breaking was detected by monitoring the time-evolution distance between the recoiling atom and the other atoms constituting the molecule.[16] The simulations of $^{131}Xe^+$ recoil in gas phase molecules used a cubic cell of 15 Å in each of the three cartesian directions, only the Γ-point was used to sample the Brillouin zone, and a plane-wave basis set cutoff of 400 eV. The simulations of $^{131}Xe^+$ recoil in radioiodine-containing molecules adsorbed on graphite used a hexagonal supercell size of a=b=19.73 Å, and c=27.0 Å, and a three-layers graphite slab with exposed (0001) facets. A three-layers slab was used because it allows to have a slab with symmetric top- and bottom-surfaces while providing an offset subsurface layer representative of the graphite structure.

Modeling of the ^{131}I transmutation event in the radioiodine-containing molecules I_2, HI, HIO, HIO_2, HIO_3, and CH_3I has been performed using *ab initio* molecular dynamics simulations. To mimic the physical and chemical consequences of ^{131}I radioactive decay, such as the emission of a β-particle leading to an ionization of the daughter nucleus (i.e. $^{131}Xe^+$) and the physical recoil of $^{131}Xe^+$, we removed one electron from the system and attributed an initial kinetic energy to the $^{131}Xe^+$ species. In the simulations, a jellium background has been used to compensate for the loss of charge. To explore the effects of ^{131}I transmutation on the molecular stability, we performed a series of AIMD simulations in which the $^{131}Xe^+$ recoils in different directions. Further, for each direction investigated, a series of simulations was carried out with a different initial kinetic energy for the recoiling $^{131}Xe^+$ species. Because an exhaustive exploration of all the possible recoil directions for a given molecule would require a considerable amount of simulation time, we have chosen to limit our investigations to directions aligned with the bonds in the molecules. This implies that the determined recoil threshold energy for bond breaking obtained is a lower limit of the recoil required to typically break a bond. This concept has been illustrated in the case of the I_2 and CH_3I molecules for which the daughter $^{131}Xe^+$ recoil has been initiated at different angles with respect to the molecular bond axis.

4.3 Results

Ab initio molecular dynamic simulations have been performed to identify the possible fragmentation products of radioiodine-containing molecules of I_2, HI, HIO, HIO_2, HIO_3, and CH_3I after for ^{131}I decay in both the gas phase (Figure 5) and adsorbed on a graphite surface. Gas phase calculations found that I_2 is the least resistant to radiolytic fragmentation, requiring 2 eV of recoil for decomposition. The HIO_x family of molecules is found to be more resilient than I_2, with a bond breaking threshold recoil energy of more than 4 eV, while HI and CH_3I molecules do not fragment after ^{131}I transmutation. Accounting for electron shake-off in methyl iodide has shown that fragmentation occurs for the doubly-ionized daughter molecule (Figure 5). Simulations of transmutation in radioiodine-containing molecules adsorbed on graphite showed that the threshold recoil energy leading to bond breaking is considerably lowered. While the identification of gas phase fragments can offer a new chemical route to consider in chemical kinetics models, we found that the formation of reactive fragment products at the graphite surface can favor their reaction with surface carbon atoms. Especially, the CH_3 and OH radicals are found to form covalent bonds with graphite which over time could potentially play a role in

reducing the number of adsorption sites of capture materials available, and hence, negatively impact their capture capability.

Figure 5: Angle-dependent threshold recoil energy to break the I—Xe bond in IXe$^+$ (a) and the C—Xe bond in doubly-ionized CH_3Xe^{2+} (b) daughter species. Different fragmentations obtained from the HIO_2 (c) and HIO_3 (d) parent molecules depending on the recoil direction and energy.

5.0 Conclusion

Electronic structure calculations have been used to determine the structure and binding energies of iodine-containing molecules to different structural components for activated carbon, including graphene-like structural elements and chemical functional groups on the edge of graphene sheets.   It is predicted that the molecules bind only weakly to graphene-like surfaces with the dominant interactions being dispersive in nature consistent with physiosorption. However, chemical reactions are possible with edge-bound functional group, although they are predicted to be endothermic in nature when those groups contain oxygen.

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6.0   Acknowledgements

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