A study of polybromide chain formation using carbon nanomaterials via density functional theory approach


Cogent Engineering (2016), 3: 1261509
A study of polybromide chain formation using carbon nanomaterials via density functional theory approach

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Abstract: We use a density functional theory approach under the local density approximation (DFT/LDA) to describe the formation of polybromide chain structures, their stretching frequency modes and charge transfer induced by the interaction of these molecules with a graphene sheet. In many cases, we find polybromides to be more thermodynamically stable than the equivalent Br2 molecular structures adsorbed on graphene sheet. This results in lower frequency stretch modes at around 170–190 cm⁻¹. We propose that these are rarely observed experimentally due to the bromination techniques used, which introduces molecular Br2 into the carbon host material. Charge transfer with their host material means that these molecules and their associated hole charge in the neighbouring carbon materials, are then coulombically repelled from other bromine molecules which acts as a barrier to combination into polybromides. Our calculated barrier for polybromide formation (2Br2 → Br4) on a graphene sheet was 0.35 eV which is an exothermic process with an enthalpy.

Received: 27 May 2016
Accepted: 10 November 2016
First Published: 17 November 2016

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PUBLIC INTEREST STATEMENT
This study explores the important problem of separation of carbon nanomaterials (e.g. carbon nanotubes, graphene, etc.). One of the approaches that can be used in the separation of these nanomaterials is by using bromine, which results in the exfoliation and/or expansion of materials such as graphite as the bromine penetrates between the layers. Bromination has been studied extensively since the 1940s as a separation technique for layers in graphite and tubes in nanotube bundles, as well as a highly effective electron acceptor to change the electrical behaviour of materials. Using atomistic computer modelling, we explore a range of structures from molecular Br2 up to extended bromine chains, both in isolation and in the presence of graphene. These extended polybromide systems such as Br4 are shown to be stable in the presence of graphene, with their own characteristic vibrational modes and electron transfer behaviour.
value of −0.28 eV. Therefore, thermodynamically, chain polybromide formation seems to be favourable but kinetically, is unlikely, since there is an activation barrier that needs to be overcome to give stable bromine chain structures.

**Subjects:** Material Science; Physics; Engineering & Technology

**Keywords:** DFT; LDA; polybromides; carbon nanomaterials

1. **Introduction**

Bromination has been studied extensively in the 1940s as a separation technique for layers in graphite and tubes, such as nanotube bundles, as well as a highly effective electron acceptor. While many experimental characterisation studies have been performed (notably Raman spectroscopy), there have only been a few theoretical descriptions of the bromination process and resultant hybrid structures reported in literature (Bulusheva et al., 2012; Strauch, Anis, & Kuntscher, 2014; Yaya et al., 2011).

There are multiple phases of the standard halides. In the gas and liquid phase, they consist of diatomic molecules. The corresponding solid halogen acid acceptor compounds (Cl₂, Br₂, I₂) belong to the space group D₂h–Cmca, with two molecules in the primitive unit cell. However, as well as the diatomic species, halides are able to form chain structures. The ability for these halides to form chains decreases in the order I > Br > Cl (Dunitz, 1973). The clusters of the heavier halogens bromine and iodine, easily form larger hetero and homo-atomic aggregates stabilized by charge delocalization. On the other hand, similar clusters of Cl and F have hardly been reported, mainly due to their high volatility and reactivity.

Polyiodide chain structures such as \( \text{I}_2^-, \text{I}_5^-, \text{I}_7^-, \) up to \( \text{I}_{29}^3- \) which results by the interactions of \( \text{I}^-, \text{I}_3^- \) and \( \text{I}_5^- \) building units, were observed in extended polymer networks (Chen et al., 1996; Lippitz, Friedrich, & Unger, 2013), with characteristic vibrational features reflected in their Raman response (Deplano, Ferraro, Mercuri, & Trogu, 1999). In addition, linear or bent chains of polyiodide consisting of several atoms have also been synthesized (Bretstovisky, Kirowa-Eisner, & Gileadi, 1986) and are significant in halogen doped organic systems in which high temperature superconducting transitions in the organic systems is associated with the iodine chains (Burns & Renner, 1991).

Polybromide chains of \( \text{Br}_2^-, \text{Br}_3^-, \text{Br}_4^-, \text{Br}_5^-, \text{Br}_8^2- \) have been characterised in various polymers and metal complexes (Jerman et al., 2008; Sharp & Gellene, 1997; Vogt, Wulff-Molder, & Meisel, 1996) and it is suggested that bromine undergoes interactions whose nature and orientation are similar to the much studied chains of polyiodides.

Recent theoretical studies suggest that at higher concentration of bromine, bromine chains could form inside SWCNTs, DWCNTs, graphite and graphene (Yaya et al., 2011). Experimental studies by Sung, Park, Park, and Hong (2007), suggest that bromine forms chains after encapsulation in SWCNTs with an odd number of bromide ions, \( \text{Br}_3^-, \text{Br}_5^- \) becoming more stable than the \( \text{Br}_2^- \) molecule. Available DFT calculations of halogen chains have been performed mainly on polyiodide chains (Sharp & Gellene, 1997), with very few theoretical calculations reported in the literature on polybromide chains, which mainly focus on geometry optimizations and electron affinity.

In this paper, we address the question of equilibrium geometry, charge transfer and stretching modes of some selected polybromide chains using ab initio DFT methods. In addition, we also attempt to reveal the particular reaction kinetics of \( \text{Br}_4^- \) chain formation on graphene sheets, which to the best of our knowledge, has not been previously examined.

2. **Methodology-computational modeling**

Ab initio total energy calculations based on pseudopotential density functional theory within the local density approximation (LDA) (Kohn & Sham, 1965) were performed on \( \text{Br}_4^-, \text{Br}_5^- \), \( \text{Br}_4^-, \text{Br}_5^- \) polybromide anion and \( \text{Br}_4^- \) interacting with graphene sheet. Supercells containing 132 atoms were
used for bromine on graphene giving the empirical formula $C_{128}Br_4$, with a large vacuum spacing of at least 26.74 Å between layers to ensure no inter-layer interaction with the next layer when the sheet is repeated in space (the isolated bromine molecule and anions were calculated as a particle in a box with a 24.99 Å cubic supercell). The method has previously been used to determine the structural configuration of intercalated impurities in graphite (Suarez-Martinez, El-Barbary, Savini, & Heggie, 2007). Atomic charge states were obtained by summing Mulliken population analysis over all the filled electronic states.

We used a localised Gaussian basis set with a large number of fitting functions per atom (22 for each C atom and 50 for each Br in order to accommodate the spatially extended polarizable charge distribution of the anionic species), with angular momenta up to $l = 2$ for C and $l = 3$ for Br. The sampling over the Brillouin zone was performed with weighted summation over wave vectors generated in the Monkhorst Pack scheme (Monkhorst & Pack, 1976), with the k-point grids chosen such that the k-point density was at least 1 k-point per $4.2 \times 10^{-4}$ Å$^{-3}$. The tolerance in the convergence of self-consistency was set as $1 \times 10^{-7}$ eV/atom, and a finite temperature electron level filling of $kT = 0.04$ eV was used as a computational tool to improve convergence. Core electrons were eliminated using norm-conserving relativistic pseudopotentials of Hartwigsen, Goedecker and Hutter (Hartwigsen, Goedecker, & Hutter, 1998), with atomic valence electron configurations of 4s$^2$ 4p$^5$ for Br and 2s$^2$ 2p$^2$ for C. The core radii of the pseudopotentials are 1.78 a.u and 1.32 a.u for Br and C respectively. A cut-off energy of 150 Hartrees was used to obtain convergence of the charge density. The calculations are performed using the density functional code, AIMPRO (Briddon & Jones, 2000; Briddon & Rayson, 2011; Rayson & Briddon, 2009). While the LDA approach does not include explicit dispersion interactions, the known over-binding of LDA compensates for this, and has been shown to give good results, for example for interlayer spacing and binding in graphite (Rob, 2003), and for molecular absorption on graphite surfaces (Adjizian et al., 2013).

All structures were geometrically optimised with no constraints of symmetry allowing both atomic positions and cell dimensions to vary freely. Optimization was not completed until forces on the atoms were less than $1 \times 10^{-3}$ eV. Vibrational frequencies were calculated by determining the energy and forces for 0.2 a.u displacements of the Bromine atoms. The second derivatives on the displaced atoms can then be found from the two-sided difference formula for the second derivative. This approach does not lead to harmonic force constants as there are quartic and higher-order correction terms in these estimates of the second derivatives. We refer to the frequencies arising from these force constants as quasi-harmonic. If all second derivatives $E_{ij}$ are evaluated, then the dynamical matrix can be found directly as $E_{ij}/(M_i M_j)^{1/2}$ where $M_i$ is the mass of the ith atom. Further discussion of this approach is given in Guiot et al. (2009), where it was successfully used to identify stretching frequencies of bromine and iodine based small molecules. The activation barrier for Br$_2$ combination is calculated using a nudged elastic band method, with seven intermediate image structures. After the end point structures have been fully optimised with no constraints, seven intermediate structures are simultaneously optimised with an additional energy constraint, in the form of a quadratic “spring” connecting an image to its two neighbours on the overall energy surface. After an initial five iterations, an additional “climbing” constraint is applied to the structure nearest the saddle point to ensure that it is constrained at the saddle point maximum.

The aim of the current study is to explore the stable ground state structures for isolated polybromide species and in the presence of graphene, their interrelation and energetic conversion barriers, and their corresponding vibronic behaviour. Further studies could later be performed using time-dependent approaches to explore optical excitations, but are not the purpose of the current study.

3. Results and discussion

3.1. Polybromide chains of $Br^-_2$, $Br^-_3$, $Br^-_4$, $Br^-_2^-_4$ and $Br^-_5$

Table 1, shows the optimised structures of different bromine anions, bond lengths and their stretching modes which were calculated and compared with literature DFT calculations and experimental...
Raman measurements (see also Figure 1). Slight charge variations could explain differences in observed modes, typically in crystals. Bond length and stretching frequencies changes dramatically with a gain in charge on the bromine molecule (Yaya et al., 2011). However, in the polybromide chains, the lower symmetry means that the charge state of each atom need not be equal and this results in different bond lengths and stretching frequencies. Atomic Br and molecular Br₂ have been characterized well both experimentally and theoretically, hence, were used here as test systems for the performance of theoretical calculations on larger clusters of Br. Calculations of Br₂⁻ stretching frequency from the literature lie below experiment values. However, our current work gave a better match to experiments. To the best of our knowledge, there is no experimental data reported for Br₂⁻ bond lengths and hence we could not make any meaningful comparisons to our calculated bond length. It should be stated however, there was a good match between other DFT calculated bond lengths of (2.81, 2.86 Å) with this work (2.83 Å).

Br₂⁻ is a metastable species resulting when two molecules of Br₂⁻ dimerize with formation energy per Br atom of (+0.42 eV) which is endothermic; making Br₂⁻ unstable compared to the other polybromide structures such as Br⁻ or Br₃⁻. The charge sits primarily on the terminal atoms, accounting for the increase in bond length that were observed after geometry optimization, which then resulted in lower stretching modes. Experimental differences in vibrational frequency exist due to the cations used to stabilize the polybromide ion, as seen in the Raman modes in Table 1. Therefore, no inference could be drawn between the calculated stretching modes with that of Raman spectroscopy, however, the bond length calculated for Br₂⁻ fits better to experiments than the other DFT calculation methods, which predicted longer bond lengths for Br₂⁻. Other factors such as basis sets and the number of k-points used, could contribute to the differences between the calculated stretching frequencies (58, 130 cm⁻¹) and that from other DFT calculations (70, 176 cm⁻¹) and also, differences may be, if the stretching frequency is highly anharmonic, since in our case the vibrations were calculated based on the quasi-harmonic approximation. Nonetheless, the error margins between the two separate theoretical works are acceptable.

Br₃⁻ polybromide anion has been seen in various geometrical structures with different levels of symmetry because of the influence of solvent interactions and crystal fields and is known to have two symmetry forms, Br₃⁻ (C₃ᵥ) and Br₃⁻ (D₅h). In this study, the asymmetric structure (linear chain; Br₃⁻ (D₅h)) and the symmetric structure (bent; Br₃⁻ (C₃ᵥ)) were optimised with calculated bond lengths and stretching modes compared with other similar data on these structures where available (see Table 1). It was found that, Br₃⁻ (D₅h), was −1.60 eV more stable than its corresponding symmetry structure, Br₃⁻ (C₃ᵥ).

Again, the calculated values are consistent with experimental and other theoretical calculations. The calculated bond angle was 180° which agrees with the other calculation methods together with the experimental bond angle of 177.3°, reported by D.D.L Chung for asymmetric Br₃⁻ (Chung, 1986).

Br₅⁻ has two symmetry forms, i.e. Br₅⁻ (C₅ᵥ) and Br₅⁻ (D₅h) and are formed when Br⁻ binds to Br₃ with a binding energy of −0.11 eV per Br. Below is the reaction describing Br₅⁻ (C₅ᵥ) formation:

\[
\text{Br}_2 + \text{Br}_3 \xrightarrow{\Delta H = -0.544 \text{eV}} \text{Br}_5^-(\text{C}_5^v)
\]

We find Br₅⁻ (C₅ᵥ), to be −0.23 eV more stable than the other symmetry form, Br₅⁻ (D₅h), which is mostly reported in Raman spectra experiments, with no experimental confirmation for the theoretically predicted stable form. Our calculation for Br₅⁻ (C₅ᵥ), agrees with similar calculations done by others in terms of the stability of this symmetry over the linear form, and the calculated bond angles of 128.4° and 173.3° closely matches that of other DFT calculations (114.6° and 177.4°) (Schuster, Mikosch, & Baur, 1998). Again, the lack of experimental data on this symmetry form makes it difficult to draw any conclusions. For Br₅⁻ (D₅h), we obtain the shorter bond length almost identical to experiment with the longer bond slightly underestimated. This is reflected in the calculated stretching frequencies with the higher frequency mode matching almost exactly experiment but the lower frequency mode slightly overestimated, as shown in Table 1.
Table 1. Comparison of calculated properties of bromine; stretching modes and bond lengths with experimental Raman modes and other DFT studies

<table>
<thead>
<tr>
<th>Bromine structures</th>
<th>( \text{Br}_2 )</th>
<th>( \text{Br}_2^- )</th>
<th>( \text{Br}<em>2^-(\text{D}</em>{\infty h}) )</th>
<th>( \text{Br}<em>2^-(\text{D}</em>{\infty h}) )</th>
<th>( \text{Br}_2^- )</th>
<th>( \text{Br}_2^-\text{C}_2 )</th>
<th>( \text{Br}<em>2^-\text{D}</em>{\infty h} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond Lengths (Å)</td>
<td>This work</td>
<td>2.29</td>
<td>2.83</td>
<td>2.55</td>
<td>2.55, 2.93, 2.93</td>
<td>2.49, 2.59</td>
<td>2.65, 2.63</td>
</tr>
<tr>
<td>Other Calc.</td>
<td></td>
<td>2.315, 2.331, 2.990, 2.964, 2.636, 2.637, 2.618, 2.593, 2.745, 3.152, 2.492, 2.756</td>
<td>–</td>
<td>–</td>
<td>2.43, 2.98</td>
<td>2.43, 2.82</td>
<td></td>
</tr>
<tr>
<td>Experiment</td>
<td></td>
<td>2.283</td>
<td>2.541–2.551</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>2.43</td>
</tr>
<tr>
<td>Calc. stretching freq. (This work) (cm(^{-1}))</td>
<td>326</td>
<td>152</td>
<td>93 (bv), 218(as), 164(sy)</td>
<td>64, 69, 72, 94, 119, 164</td>
<td>58, 130</td>
<td>16, 80, 81, 84, 90, 144, 174, 221, 227</td>
<td>184, 242</td>
</tr>
<tr>
<td>Previous DFT calculations (cm(^{-1}))</td>
<td>313, 321, 312, 118, 121, 179</td>
<td>84, 86(bv), 176, 178(as), 146, 152(sy), 81(bv), 216(as), 158(sy)</td>
<td>(99, 106, 155.9, 102, 158.2)</td>
<td>70, 176</td>
<td>(16.2, 74.4, 76.4, 82.5, 83.5, 122.8, 133, 192.8, 218)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Experimental Raman modes (cm(^{-1}))</td>
<td>320, 325</td>
<td>149–160</td>
<td>210, 205, 201(as), 170, 163, 160(sy), 140(sy), 208(as)</td>
<td>–</td>
<td>(74, 167), (187, 200)</td>
<td>(157, 245)</td>
<td></td>
</tr>
</tbody>
</table>

Notes: bv = bending vibration, as = asymmetric stretch, sy = symmetric stretch.

*Schuster et al. (1998).
3Erbil, Dresselhaus, and Dresselhaus (1982).
4Wight, Ault, and Andrews (1976).
5Novoa, Mota, and Alvarez (1988).
6Huber and Herzberg (1979).
7Evans and Lo (1967).
8Estienne (1986).
9Aragoni et al. (2005).
12Clark, Maresca, and Puddephatt (1968).
13Chung (1986).
Thus, where comparable data is available, it appears that we are able to accurately model polybromide anions, generally reproducing experiment better than previous theoretical results. We next turn our attention to their formation and interaction with graphene.

3.2. Kinetic barrier for Br chain formation

Even though extensive progress has been made in the determination of structures and transitional phases in graphite-bromine at or above room temperature with many experimental and theoretical data, a lot remains to be answered concerning what happens to graphite-bromine at high concentration and low temperatures. The existence of polybromides chains was reported experimentally by D.D.L. Chung et al. who proposed the chain of polybromides at liquid nitrogen temperature in her work on graphite-bromine intercalates (Chung, 2002).

Suzuki, Yokohama, and Ito (1929), carried out Raman vibrational spectroscopy for bromine chains at 77K and reported frequencies as low as (110, 96, 82, 70, 53 cm$^{-1}$). The lowest temperature Raman frequency measurement in the literature was carried out at 15 K, in which frequencies for solid bromine were given as (55, 74, 86, 101 cm$^{-1}$), by Cahill and Leroi (1969).

We are not aware of theoretical calculations confirming these polybromides chains with carbon at low temperatures. Therefore, this section of the paper is aimed at giving insight on these complexes and unclear processes occurring during the formation of these structures.

Table 2. Calculated parameters for graphene interacting with Br$_4$ and 2Br$_2$ during the formation of chain structures

<table>
<thead>
<tr>
<th>Calculated parameters</th>
<th>Br$_4$ on graphene</th>
<th>2Br$_2$ on graphene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br-Br bond length (Å)</td>
<td>2.4, 2.6</td>
<td>2.33</td>
</tr>
<tr>
<td>Br-C distance (Å)</td>
<td>3.3</td>
<td>2.70</td>
</tr>
<tr>
<td>C-Br-Br bond angle (°C)</td>
<td>70.3</td>
<td>180</td>
</tr>
<tr>
<td>Stretching frequency (cm$^{-1}$)</td>
<td>175</td>
<td>284</td>
</tr>
<tr>
<td>Charge transfer/Br (e)</td>
<td>0.3</td>
<td>0.2</td>
</tr>
</tbody>
</table>
An optimised geometry (see Figure 2) of bromine molecules on graphene was obtained by placing two molecules of bromine at a distance of 11.28 Å apart on a graphene sheet, Table 2.

Thermodynamically, a reaction in which two molecules of bromine sitting at a distance of 11.28 Å apart on graphene sheet and perpendicular to each other, will gradually align into chains of Br₄ polybromide ions with an increase in bond length and a decrease in vibrational stretching mode as a result of charge transfer, but, kinetically this seems restricted, due to the presence of a kinetic barrier.

While, the formation of chain structures is favourable, there is a barrier (activation energy) for the two bromine molecules to stick together in forming this chain which was calculated as 0.35 eV. This is due to a longer range Coulombic repulsion of associated holes in graphene beneath the Br₂, and Coulombic repulsion between the Br₂ themselves at shorter distance. This transformation is exothermic, in which the enthalpy of formation for the reaction was calculated as; ΔH = −0.28 eV, as shown in Figure 3. We initially studied many polymerised Br structures in graphite, often by starting from cells with too high Br density. All calculations of Br vibrational modes were consistent with the values reported in Table 2, i.e. in the range 170–190 cm⁻¹. This stretch frequency therefore seems to be characteristic of polymerisation in the C-Br system. The charge transfer induced by chains appears to be greater, per bromine, than that associated with molecular Br₂.

4. Discussion and conclusions
In this current study we calculate the structure and vibrational modes for a range of small polybromide species. Excellent agreement with experiment is found for Br₂, Br⁻₂ and Br₃. More extended species such as Br₄ also appear to be possible and energetically favoured on graphene surfaces as compared to isolated Br₂, but we find a small energy barrier to Br₄ formation.

It is interesting to speculate from this whether polybromide chains may be common in carbon nanomaterials. Notably, polyhalide analogues of bromide, have been observed in brominated polymers and there is indirect evidence that such chains may also exist in some brominated carbon nanomaterials. The formation of polybromide chains from Bromine pairs is favourable but due to Coulombic repulsion of associated holes in graphene, this is kinetically hindered. For the polybromide chains, longer bond lengths and low stretching frequency mode were observed.

The total charge transfer for 2Br₂ is 0.4e compare 1.2 e for Br₄ resulting in stronger electrostatic interaction between Br₂ and graphene. This therefore, resulted in a shorter interlayer distance for the Br₂ in graphene than that of the Br₄.
Yaya et al., Cogent Engineering (2016), 3: 1261509
http://dx.doi.org/10.1080/23311916.2016.1261509

Funding
A. Yaya is grateful for the financial support received from the Pays de la Loire region, France, and the Institute de Matériaux (IMN), University of Nantes, France, where much of this work was carried out. A. Yaya acknowledges support from the Office of Research, Innovation and Development (ORID), University of Ghana (grant number URF7/029/2013-2014). C.P. Ewels acknowledges EU IRSES Project 612577 “NanoCF” for financial support.

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Citation information

Cover image
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