Bromination of Graphene and Graphite

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We present a density functional theory study of low density bromination of graphene and graphite, finding significantly different behaviour in these two materials. On graphene we find a new Br₂ form where the molecule sits perpendicular to the graphene sheet with an extremely strong molecular dipole. The resultant Br⁺-Br⁻ has an empty π-orbital located in the graphene electronic π-cloud. Bromination opens a small (80meV) band gap and strongly dopes the graphene. In contrast, in graphite we find Br₂ is most stable parallel to the carbon layers with a slightly weaker associated charge transfer and no molecular dipole. We identify a minimum stable Br₂ concentration in graphite, finding low density bromination to be endothermic. Graphene may be a useful substrate for stabilising normally unstable transient molecular states.

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The intercalation of carbon nanomaterials with electron donors and acceptors is an active research area in which much effort is channelled towards the understanding and controlling of the electronic properties of graphene and graphite. Numerous potential applications such as sensors, electronic display panels, hydrogen storage and supercapacitors have been suggested for such intercalated materials. The layered structure of graphites plays an important role in charge transfer reactions. Acceptor species can intercalate between graphitic layers, expanding the graphite with the resultant hybrids known as graphite intercalated compounds.

Bromine acts as an acceptor when intercalated in materials such as graphite or nanotubes, and has been proposed experimentally as a way to open a band gap in 3- or 4-layer graphene. The in-plane electrical conductivity of graphite increases from 2.4 × 10⁶ Ω⁻¹ cm⁻¹ at room temperature to 2.2 × 10⁸ Ω⁻¹ cm⁻¹ after intercalation with bromine.

Bromine forms many ordered phases in graphites and undergoes an order-disorder phase transition as the amount of bromine or temperature change. Bromine intercalated graphite forms stage-n compounds where n is the number of graphitic layers between planes of Br₂ (n > 10). Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy at room temperature and 100 K showed that intercalated bromine molecules lie parallel to the basal plane, with an expansion of the Br-Br distance by 0.03 Å to accommodate the lattice mismatch between the free molecule and the 2.46 Å spacing between graphite hexagons. X-ray diffraction and electron microscopy studies suggest that intercalated Br₂ at lower concentration is composed of chains of Br₂ molecules in which the intermolecular distances is identical to that of solid bromine.

Graphite Raman spectra associated with Br₂ intercalation show a strong peak at 242 cm⁻¹ assigned to the intercalated Br₂ stretch mode. The frequency is downshifted from 320 cm⁻¹ for gaseous Br₂ and 295 cm⁻¹ for solid molecular bromine. There have been limited density functional studies of brominated graphite and graphene.

In this paper we examine low density bromination of graphene and graphite using density functional (DFT) calculations within the local density approximation. The method has been successfully used to study intercalated boron in graphite. A localised Gaussian basis set is used with a large number of fitting functions per atom (22 for each C atom and 50 for each Br), with angular momenta up to l=2 for C and l=3 for Br. A finite temperature electron level filling of kT=0.04eV is used to improve convergence. Core electrons were eliminated using norm-conserving relativistic pseudopotentials of Hartwigsen, Goedecker, and Hutter. A cut-off energy of 150 Hartrees was used to obtain convergence of the charge density.

Isolated Br₂ was calculated in a 13.23 Å cubic supercell. Hexagonal 4 × 4 graphene supercells containing C₃₂Br₂ were used with a large vacuum spacing of 31 Å between layers to ensure no inter-layer interaction, and a 4 × 4 × 1 Monkhorst-Pack k-point grid. Graphite calculations used 3 × 3 × n layer supercells (C₁₈₄₃(Br₂)ₙ, n=1-4, m=1-2) for different layer stackings, with 4 × 4 × 1 or 4 × 4 × 2 k-point grids depending on cell size. All structures were fully geometrically optimised with no constraints of symmetry, allowing both atomic positions and cell dimensions to vary freely. Atomic charge states were obtained by summing Mulliken population analysis over all the filled electronic states. Vibrational frequencies were calculated by determining the energy and forces...
for ± 0.2 au 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 derivatives on the displaced atoms. All results are spin averaged, tested calculations with spin polarisation all gave zero spin solutions. All results are quoted in eV (binding energy of Br₂ in structure (a) is 0.40eV). The text refers to (a) Br₂∥ and (d) Br₂⊥.

Table I. Calculated parameters for the most stable Br₂∥ and Br₂⊥ on graphene compared with literature DFT calculations.

| Orientation / Br₂ (eV) | Br₂∥ | Br₂⊥ | Literature |
|------------------------|-------|-------|------------|
| Binding energy / Br₂ (eV) | -0.40 | -0.29 | Parallel |
| Br-Br Stretch Frequency (cm⁻¹) | 288 | 270 | 31 |
| Br-Br bond length (Å) | 2.33 | 2.31 | 2.243 |
| Br-C distance (Å) | 2.74 | 3.45 | 3.7 |
| Charge state of Br atoms (e) | +0.48 | -0.04 | +0.02 |
| Total Charge transfer / Br₂ (e) | -0.13 | -0.08 | -0.02 |

The most thermodynamically stable arrangement is Br₂∥ oriented perpendicular to the graphene sheet above a carbon atom (Figure 1), referred to hereafter as Br₂∥. Its binding energy of 0.40eV shows it will be strongly physisorbed at room temperature. However the small variations in binding energy between structures suggests that low density Br₂ binding to graphene will be largely orientation independent; indeed and at these densities at room temperature Br₂ should be in constant tumbling motion (this also holds for the results of[27]). Increasing Br₂ concentration did not significantly change the relative energies of perpendicular and parallel orientations. However it is possible to obtain twice the maximum surface density for Br₂∥ as for Br₂⊥ in the parallel orientation (Figure 1, referred to hereafter as Br₂⊥). Thus for the limit of high surface concentrations we expect Br₂∥ to dominate.

Br₂∥ represents a very unusual configuration for bromine. It shows strong charge transfer (0.129e) from the graphene, with a very strong induced molecular dipole (Br⁺0.480-Br⁻0.609). The singly occupied p-orbital of the lower Br atom depopulates into the p₂ of the upper Br atom forming a nascent Bromonium and Bromide ion pair. In this way the emptied lower p₂-orbital can sit within the graphene π-cloud (Br only 2.74 Å above the graphene).

This behaviour is reminiscent of the well-known reaction between Br₂ and unsaturated bonds in organic chemistry. However in these cases this dipolar form of Br₂ is an unstable transient state that immediately saturates the C=C bond, forming two Br-C bonds. In graphene this final step would be endothermic due to steric hindrance between the Br atoms as a result of the mechanical confinement of the lattice. Indeed our attempts to stabilise C-Br pairs on graphene in both neighbouring (1,2) and cross-hexagon (1,4) configurations both resulted in Br spontaneously reconstructing into a Br₂ molecule (placing Br-C in a (1,4) configuration with Br atoms on opposite sides of the graphene is 1.68eV less stable than Br₂∥).

The unusual Br₂∥ configuration is reflected in the band structure (Figure 2a). The strong coupling between the graphene LUMO and the Br₂ antibonded state at around +0.6 eV reflects the interaction between the empty Br p₂-orbital and the graphene π-cloud, with the resultant low density Br₂ layer opening a small 86meV band gap.

In contrast Br₂⊥ has no induced dipole, with weaker charge transfer (0.084e) from the graphene. The molecule sits 3.254 Å above the graphene i.e. above the π-cloud, with the additional charge occupying the Br₂ ppσ* anti-bonding state. The band structure (Figure 2b) shows the Br₂ states lie lower than those of Br₂∥ by ~0.7eV. The Br₂ anti-bonded state pins the Fermi level ~0.2eV lower than in the pristine case, leaving graphene states around the K-point depopulated, indicating charge transfer from graphene to Br₂. The Bromine states are flat and largely decoupled from the graphene bands since there is only weak interaction between Br₂ orbitals and the graphene π-cloud in this orientation.

Our results are consistent with experimental Raman observations of brominated graphene[28]. While for
graphene with three or more layers a resonant Raman signal was observed for Br$_2$ at around 240cm$^{-1}$, for mono- and bi-layer graphene no bromine signal was observed. This could be an orientation effect, since if the Br$_2$ sits perpendicular to the surface as we propose and orthogonal Raman is used, then the molecules will be aligned with the beam and there will be no interaction and hence no signal. In addition the bromine HOMO/LUMO states are further apart for Br$_2$ than for Br$_2$ or the various graphite structures we have examined (1.7-2.0eV). Given the excitation laser used (633nm, 1.96eV), or the various graphite structures we have examined (1.7-2.0eV), this may not be in resonance as the authors suggested. We note that the strong dipole of Br$_2$ would have an associated Raman signal, and since none is observed this allows us to exclude this configuration. We note that the strong dipole of Br$_2$ will make the molecule infra-red active.

We now turn our attention to graphite. Our calculated energy to separate AB graphite layers is 36.7 meV/atom, with AA stacked graphite 12.0meV/atom less stable than AB stacked graphite. These figures are in good agreement with experiment (35meV/atom$^{13}$) and previous calculations (9.68-9.70meV/atom$^{26}$). Our interlayer spacings of 3.39Å and 3.50Å for AB and AA-stacked graphite respectively are also in reasonable agreement with previous calculations.$^{25}$

We placed Br$_2$ in a variety of different orientations and locations including above $\alpha$- and $\beta$- carbon atom sites and hexagon centers, in graphite of various layer stackings. Unlike graphene, Br$_2$ in graphite is more stable parallel to the graphitic layers with Br atoms above hexagon centers (see Table I), in agreement with experiments.$^{6,9,12,26}$ Perpendicular oriented Br$_2$ structures are much less stable (by typically 0.52eV). The results are summarised and compared with experiment in Table II. We note that the charge transfer value from Raman was reported with a large uncertainty.$^{13}$

Besides the lowest energy structures quoted here we obtained many metastable structures. While their energies were all within 0.01-0.05eV of those structures discussed here, they show significant variation in the Br$_2$ stretch frequency (250-278cm$^{-1}$), and slight variation in position and Br-Br bond length (2.31-2.33Å). This suggests that at room temperature Br$_2$ in graphite will be mobile, and is consistent with the observation of a broad and somewhat complicated Raman peak.$^{11}$

We explored all possible layer stacking combinations for stage-1 and stage-2 intercalated graphites. Bromine molecules are most stable with AA-stacked graphite each side, while unbrominated graphite layers preferentially are AB stacked. Thus (indicating layers of bromine molecules by X) we find the most stable stage-1 phase to be [AX]$_n$, and stage-2 to be [AXAXB]$_n$, suggesting [AXAB]$_n$ and [AXABABXBAB]$_n$ for stage-3 and stage-4 respectively.

Our calculated bromine intercalation energy is weakly endothermic, since at these low densities the energetic cost associated with separating graphite planes (a cost per unit area) is not sufficiently offset by the binding energy of Br$_2$ to the layers. Subtracting the energy to separate graphite layers from the Br$_2$ intercalation energy gives an energy for intercalation of Br$_2$ into ‘pre-separated stage-1 graphite’ of 0.581eV/Br$_2$. This implies that the minimum Br$_2$ concentration for exothermic intercalation in stage-$n$ graphite will be C$_{16n}$Br$_2$. Indeed

![FIG. 2. Band structure of (a) Br$_2$ and (b) Br$_2$ on graphene (eV), faded dotted lines indicate the same supercell of pristine graphene for comparison. Arrows indicate bromine related states.](image)

### Table II. Calculated and experimental results for Br$_2$ intercalated graphite.

| Cell used          | Stage-1 | Stage-2 | Experiment |
|--------------------|---------|---------|------------|
| C$_{16}$Br$_2$     | +0.08   | +0.08   |            |
| Binding Energy/Br$_2$ (eV) | 6.45 | 6.47 | 7.0$^{11}$  |
| C-C layer distance (Å) | 9.80 | 9.82 | 10.70 |
| $c$-axis (Å)       | 2.30 | 2.30 | 2.34$^{10,12}$ |
| Br-Br bond length (Å) | 3.51 | 3.46 | 2.97 |
| Br-C distance (Å)  | 287  | 274  | 242-258$^{11,13}$ |
| Br-Br frequency (cm$^{-1}$) | -0.10 | -0.12 | -0.11$^{12}$ -0.34$^{13}$ |

- Translation quality: 100
- Language quality: 100
- Coherence quality: 100
- Conversational quality: 100
a fixed-Br calculation for a C₄Br₂ stage-1 high coverage structure gives Br₂ intercalation as exothermic. Thus Br₂ will aggregate in the same inter-layer space and should be considered as a layer rather than individual molecules.

This minimum required concentration also suggests intercalation will be a slow diffusion process with an abrupt diffusion front. This is consistent with long experimental intercalation times despite the high bromine inter-layer mobility. It also explains why, on out-gassing bromine, the material switches from a stage-2 to compound to stage-n (n=3, 4, ...) rather than remaining stage-2 with lower bromine density per layer.  

We note that frequency calculations incorporating the energetic double derivatives of surrounding carbon atoms gave identical values to within 1 cm⁻¹, showing that the Br₂ stretch mode is decoupled from the surrounding carbon lattice consistent with the literature.  

Band structure calculations of Br₂ layers between graphite sheets (not shown here) give a bromine-related state which pins the Fermi level just below that of perfect graphite (~0.1eV) indicating charge transfer from graphite to Br₂. This state shows some dispersion indicating weak coupling with the underlying graphite. In other respects the graphite band structures are barely perturbed.  

Our results on graphite and graphene can explain the anomalously large G peak shift for single graphene sheets in comparison with few-layer graphene. Since the higher maximum Br₂ surface density for Br₂⁺ than for inter-layer Br₂ means charge transfer per unit area will be higher. Additionally Br₂ can attach to both sides of graphene. We find a binding energy of -0.38eV /Br₂ for two Br₂⁺ either side of the same C atom, with associated charge transfer of -0.12e/Br₂. Thus the net total charge transfer per unit area will indeed be significantly higher for monolayer graphene than multi-layer systems.  

Test calculations for a (5,5) single walled nanotube, either isolated or in bundles, gave similar structural behaviour, i.e. Br₂ on the surface of the isolated tube adopts a perpendicular orientation, while intercalated Br₂ sits parallel to the tube walls. This will be explored further in a later publication.  

In summary, we have examined low density Br₂ adsorption in graphene and graphite. On graphite Br₂ adopts an unusual perpendicular orientation, opening a small band gap (~86meV) in the graphene with strong charge transfer. The molecule forms a Br⁺+Br⁻ pair, rendering it infra-red active. This is a new form of Br₂ previously only considered as an unstable intermediate to bromine induced carbon bond saturation. Such graphene-induced stabilisation behaviour may be mirrored in other molecular species, enabling study of otherwise unstable reactive molecular forms.  

In graphite Br₂ adopts a parallel orientation to the sheets with an associated charge transfer. Our calculations are in good agreement with experimental data where available. At high bromine concentrations and low temperatures there is some evidence of bromine chain structure formation in graphite, and we are currently investigating this further. We note that high density bromination of graphite leads to stage-2 compounds, and in conjunction with an appropriate secondary surfactant this may be a promising way to produce bilayer graphene.

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