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Vibrational properties of water retained in graphene oxide

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ABSTRACT

Vibrational properties of water molecules retained in the interlayer space of graphene oxide were studied by combining inelastic neutron scattering spectroscopy with density functional theory calculations. The credibility of Lerb–Klinowski model in the description of the amplitude weighted vibrational density of states has been successfully examined. The solid-state plane-wave DFT computations have delivered satisfying qualitative interpretation of the INS spectrum, which was found to be mainly driven by the vibrational dynamics of the retained water.

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1. Introduction

As we enter the 21st century, there has been a tremendous activity in the field of basic and applied graphene oxide (GO) research. A sizable fraction of this effort has been focused on the exploitation of the structural properties which have been the subject of considerable debate over the years. However, even to this day no unambiguous model of GO exists.

The most recent GO models have rejected lattice-based description and have focused on its nonstoichiometric, amorphous alternative. Now it is generally accepted that GO mostly contains hydroxyl (–OH) and epoxy (–O–) groups spread over its basal planes [1]. The most widely accepted model is the one by Lerb and Klinowski, who have published several papers regarding the structure and hydration behavior of GO as studied by solid-state nuclear magnetic resonance (CP MAS NMR) [2,3]. In the papers, which are in fact the most widely cited in the contemporary literature, it was found that there is significant interplatelet hydrogen bonding through the alcohols and epoxide functional groups, contributing to the stacked structure of GO.

Many papers considering theoretical modeling of GO have been published in recent years. Both computational approaches – the molecular and periodic ones – have been found to be equally applicable. The computations have been successfully applied for exploring different aspects, including mechanical (e.g. Young's modulus) [4], electronic or chemical properties (e.g. Fukui Functions) [5]. There were also extensive theoretical studies of solid-state NMR [6] and vibrational spectroscopy. The most recent attempts were

presented in example by Page et al. [7], delivering very successful report in frame of molecular modeling by combining DFT with Tight-Binding approach. Recently, Liu et al. have presented extensive optical vibrational analysis of epoxy graphene oxide by means of periodic Local Density Approximation (LDA) computations [8].

The most recent studies have further adjusted Lerb–Klinowski model. We should mention the excellent Car–Parinello molecular dynamics simulations, recently published by Kim et al. [9]. The authors have found that only the presence of epoxy and hydroxyl groups on the basal planes is expected in the thermodynamic stable GO systems. The origin of the chemical and kinetic stability of graphene oxide has been recently further explored in [10]. The presence of the hydrogen atoms on the basal planes of freshly synthesized GO sheets expresses its metastability. As a result, it evolves to the stable form by recombination of the hydrogen atoms with epoxy and hydroxyl groups, being a source of water molecules, which are thus always present in graphene oxide materials.

Hence, it is interesting to focus on the vibrational properties of the retained water, where inelastic neutron scattering spectroscopy is the method of choice. Many papers exploring the optical vibrational spectroscopy of GO frameworks have been already published. However, the only neutron scattering studies were presented by Buchsteiner et al. [11,12]. The authors have focused on the vibrational dynamics of the interlayer water at the higher temperature range (220–320 K), claiming that a more detailed study of the density of states is expected in the future [11]. Unfortunately to the best of our knowledge, there were no attempts of simulating the INS spectrum of GO published so far. As inspired by the Buchsteiner's work, we present the simulations of the low-temperature INS spectrum of GO in frame of density functional theory calculations based on the Lerb–Klinowski model.

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The neutron scattering measurements of GO were performed at 20 K on NERA time-of-flight inverted-geometry spectrometer at the high-flux pulsed neutron source IBR-2 [13]. The graphene oxide sample was synthesized by Tkachev et al., at the Institute of General and Inorganic Chemistry RAS in Moscow, by a modified Hummers method [14]. The experimental spectra have been recently presented in [15]. Further experimental results and details of the neutron scattering investigation of GO and reduced GO materials, which were synthesized at different laboratories, will be presented elsewhere [16].

2. Theoretical computations

2.1. Model preparation

The main problem with the construction of an acceptable GO model is related to the fact that the considered system is non-stoichiometric and amorphous by its nature. Any experimental information can be treated only as a statistically averaged global value. Hence, one cannot precisely define the dimension of the cluster nor the stoichiometry at the microscopic level. Moreover, the reality is further complicated by presence of defects and water molecules in between the layers. Hence, we proposed two different microscopic models, namely (a) the cluster approach and (b) more systematic periodic model – neglecting the dangling atoms and trying to mimic the water influence in frame of short-range ordering revealed by the neutron diffraction experiments [16].

- (a) In the first case, we simply built an arbitrary Lorf–Klinowski model. The single GO sheet (see Figure 1 (a)) is built by benzenoid rings in 5×5 dimension. The epoxy ($\times 11$) and hydroxyl ($\times 8$) groups are randomly spread over both sides of the basal planes, while the carboxyl groups ($\times 2$) along with the hydrogens ($\times 21$) are terminating the cluster. The system is presented in Figure 1 a. The single-sheet model was extended into the double-layer (Figure 1 (b)) and ‘solvated sandwich’ (including 48 H_2O) (Figure 1 (c)) models.
- (b) The periodic system was partially based on the Lorf–Klinowski model as considered by Liu et al. [8]. In the quoted paper, the single-layer system is characterized by 50/50 relation of carbon atoms with sp^2 and sp^3 hybridization, where OH/O ratio equals 2.00. The layer includes 40 benzenoid rings in the 8×5 dimension. Due to the electronic energy convergence problems, we slightly modified the model by removing two epoxy groups and recombining two hydroxyls. Hence, our single layer consists of 20 hydroxyl and 8 epoxy groups (Figure 1 d – bottom). The distribution of the functional groups did not cause possible overlapping of the periodic images. In contrast to the single-layer periodic model proposed by Liu, we considered the double-sheet case (Figure 1 d – top) with the typical layer spacing of 7 Å, as we found experimentally [16]. Due to the enormous size of the system and very subtle intermolecular interactions relations, we put special attention to the pre-optimization process so as to avoid the imaginary frequencies in the vibrational analysis. We pre-optimized the initial cell structure with Density Functional Theory based Tight Binding (DFTB) approach [17] as implemented in DFTB+ program [18,19]. The Slater–Koster parameters were derived from PBE/DNP calculations [19]. The structural pre-optimization was followed by further described plane-wave DFT computations.

The solvated structures were prepared by distributing water molecules (4, 8, 12, 16, 20 and 24) equally from both sides of

the layers. In order to provide a justified random distribution, the structures were annealed at 1500 K and simple room-temperature molecular dynamics runs (1500 ps with 1 fs step) were performed in NVT ensemble. The computations were done with Forcite program using Dreiding force-field [20]. Only water coordinates were unfrozen during the simulations, while the formation of hydrogen-bonds was unconstrained.

Figure 1f compares the calculated percentage mass ratios for all the models included in the computations along with the experimental results of the elementary analysis as presented in [14]. The closest agreement with the experimental data is reached by the periodic model including 24 H_2O molecules.

2.2. The computational methodology

In order to understand the INS spectra, we performed the atomistic simulations in frame of Density Functional Theory [21,22], using (a) molecular modeling and (b) periodic boundary conditions (PBC) approach.

In both cases, the Generalized Gradient Approximation (DFT) of the exchange–correlation functional was applied, employing the Perdew–Burke–Ernzerhoff (PBE) functional [23,24] revised by Hammer (rPBE) [25]. The revised rPBE functional, also known as hard GGA, was originally introduced to improve the adsorption energetics, being out of interest of the vibrational spectroscopy community. However, we have recently found its credibility in vibrational calculations.

- (a) We applied molecular modeling using DMOL3 program [26,27] and DND numerical basis set, generally comparable with the standard 6-31G(d) level. We used fine electronic convergence criteria as defined in Materials Studio [19]. The precisely optimized equilibrium geometries were followed with the vibrational analysis performed using finite displacement method.
- (b) Alternatively, the periodic boundary conditions computations were performed using plane-wave pseudopotential method implemented in CASTEP version 6.1 [28,29]. The computations were performed using designed nonlocal norm-conserving pseudopotentials (NC) [30]. Due to enormous size of the studied system, the computations were done in good compromise between the numerical accuracy and overall computational performance. The plane wave kinetic energy cut-off energy of 750 eV was used along with the standard density grid settings. Due to the studied system size, the electronic k-point sampling was limited to the Γ point. The fixed-cell geometry-optimization was performed with the convergence criteria for the total energy, maximum force, maximum atomic displacement and SCF iterations smaller than 5×10^{-7} eV/atom, 0.0025 eV/Å, 5×10^{-5} Å and 1×10^{-9} eV/atom, respectively. The phonon frequencies at Γ were obtained by diagonalization of dynamical matrices computed using density functional perturbation theory (DFPT) [29], where the acoustic phonon sum rule (ASR) $< 25 \text{ cm}^{-1}$ was imposed. The analysis of the resulting eigenvectors was used in tentative assignment of the computed phonons. From the computed eigenfrequencies and eigenvectors, the inelastic neutron scattering fundamental intensities were predicted with the help of aClimax program [31]. The spectral shape was further approximated by convolution of the calculated intensities with the spectral resolution of NERA spectrometer [32] and/or uniform Lorentzian broadening (20 cm^{-1} width at half maximum).

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