



An empirical force field for the simulation of the vibrational spectroscopy of carbon nanomaterials



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ARTICLE INFO

Article history:

Received 20 September 2016
Received in revised form
19 November 2016
Accepted 22 November 2016
Available online 24 November 2016

Keywords:

Raman spectroscopy
Force field
Carbon nanotubes
Graphene

ABSTRACT

An empirical force field for carbon based upon the Murrell-Mottram potential is developed for the calculation of the vibrational frequencies of carbon nanomaterials. The potential is reparameterised using data from density functional theory calculations through a Monte-Carlo hessian-matching approach, and when used in conjunction with the empirical bond polarisability model provides an accurate description of the non-resonant Raman spectroscopy of carbon nanotubes and graphene. With the availability of analytical first and second derivatives, the computational cost of evaluating harmonic vibrational frequencies is a fraction of the cost of corresponding quantum chemical calculations, and makes the accurate atomistic vibrational analysis of systems with thousands of atoms possible. Subsequently, the non-resonant Raman spectroscopy of carbon nanotubes and graphene, including the role of defects and carbon nanotube junctions is explored.

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1. Introduction

Since their discovery, carbon nanotubes (CNTs) [1] and graphene [2] have been the subject of considerable research interest owing to their unique structural, mechanical and electronic properties. Raman spectroscopy has emerged as one of the most popular techniques used to study these systems, providing information on the structure, bonding and environment of CNTs [3] and graphene [4], including details on CNT diameter, chirality and defects. Key modes in the Raman spectroscopy of CNTs are the G band and the radial breathing mode (RBM). The G band arises from planar vibrations of the carbon atoms and is the most intense band, and is present in both graphene and CNTs. For CNTs this band can split into the G^+ and G^- bands, which correspond to in-plane movements along and perpendicular to the CNT axis, respectively. The G band can be used to determine whether a CNT is metallic or semi-conducting, and allows for the qualitative assignment of the chiral indices of a CNT. The RBM corresponds to the coherent expansion and contraction of carbon atoms in the radial direction, and the frequency of this mode is known to depend on the diameter of the CNT. A further very weak band is the disorder-induced D band, which is associated with sp^3 defects in CNTs [5].

Although Raman spectroscopy is used routinely to study CNTs and graphene based materials, the prediction of the Raman spectroscopy of these systems is a challenge for computational methods. The accurate calculation of the vibrational frequencies and associated spectroscopy of carbon nanomaterials can potentially aid the interpretation of experimental measurements and allow the relationship between the molecular structure and the observed features to be explored. Simulation of vibrational spectroscopy using quantum chemical methods, such as density functional theory (DFT), is well established. However, the computational cost of these methods makes them impractical for the study of large systems such as CNTs. This can be overcome for the simulation of pristine nanotubes through the use of periodic boundary conditions, but the use of periodic boundary conditions to study realistic CNTs that are non-uniform and contain vacancies and defects is limited since such calculations would require large unit cells. Furthermore, periodic boundary conditions are not suitable for studying systems such as nanotube junctions which are inherently non-periodic.

Several groups have reported DFT based harmonic frequency calculations of the infrared (IR) and Raman spectroscopy of fullerenes, including C_{60} and C_{70} [6–10]. Similar calculations have also been performed for related systems such as [n]cycloparaphenylenes [11,12] and a nanotorus [13]. DFT calculations have been used to study the Raman spectroscopy of zigzag nanotubes of varying diameter [14], accurately reproducing the diameter

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dependence of the RBM, although these calculations only considered one unit cell capped with hydrogen atoms. Such small model systems would not be expected to describe other bands such as the G band accurately. Another study employed DFT to study the vibrational spectroscopy of ultra-small diameter nanotubes [15]. Yumura et al. reported DFT calculations of the vibrational frequencies of relatively large nanotubes, consisting of up to 120 carbon atoms, and studied the effects of the end caps on the spectra [16]. Recently the Raman spectroscopy of zigzag nanotubes with length of up to 2.15 nm was studied using DFT, with larger tubes studied using a cartesian coordinate transfer technique [17]. The calculations reproduced the dependence of the frequency of the RBM on the tube diameter, but larger tubes were required to describe the G band modes accurately. It was found that the G band was more sensitive to the presence of defects, and there was a reduction in the intensity of the RBM on the introduction of a Stone-Wales (SW) defect. These studies represent the current limit of what can be achieved through direct non-periodic DFT calculations. The Raman spectroscopy of nanotubes including the effect of SW and di-vacancy defects on the spectra has been studied [18] using plane-wave based periodic DFT with the Raman intensities computed using the empirical bond polarisation model (BPM) [19]. The BPM is an example of a computationally inexpensive approach to evaluating Raman intensities and other related approaches have been reported and used to study the Raman spectra of liquids [20]. Other work has studied the effect of the Raman excitation profile for CNTs under torsion or uniaxial strain [21]. Computationally less expensive methods that have been applied to study the vibrational spectroscopy of CNTs include tight-binding DFT, which has been applied to study the vibrational spectra of fullerenes [22,23], and force constant based methods [24–27]. Calculations of the resonant Raman spectroscopy of CNTs using a non-orthogonal tight-binding model have been reported, and the influence of point defects on the spectra studied [28,29].

Ideally it would be possible to model the vibrational spectroscopy of these systems efficiently without the constraints of periodicity, providing an accurate description of experiment and opening the opportunity for the role of edges and defects to be explored. Empirical potentials provide a possible solution to this problem. The attraction of this approach for studying the vibrational spectroscopy of these systems is evident by comparing the associated computational cost with a DFT calculation. On a single processor, a B3LYP/6-31G* calculation of the harmonic frequencies of C₆₀ and C₇₀ requires over 40,000 and 60,000 s, respectively. Similar calculations using the empirical Murrell-Mottram potential take two and three seconds, representing a many thousand-fold decrease in computational time. Furthermore, the use of empirical potentials alleviates the memory requirements of using quantum chemical methods, allowing systems of thousands of atoms to be studied routinely. However, for empirical potentials to form viable methods for simulating the vibrational spectroscopy of these systems, the accuracy of quantum chemical methods needs to be retained.

The prominence of carbon-carbon interactions in chemistry, physics and materials science has led to the introduction of several highly developed empirical potentials. Bond order potentials that can describe changes in hybridization and the breaking and formation of bonds are one of the most popular types of potential. These include the Reactive Empirical Bond Order (REBO) potential [30], which is a development of the Brenner potential [31] which was based on the Tersoff potential [32], and more recently the Reactive Force Field (Reaxff) potential was introduced [33]. The Raman spectroscopy of nanotube junctions have been studied

based upon the REBO potential [34]. Several other simpler potentials for carbon have been reported in the literature including the TLHT potential of Takai et al. [35] and the potentials of Murrell and co-workers [36–38]. Within the context of computing vibrational spectroscopy, one of the advantages of these mathematically simpler potentials is that it is relatively straightforward to implement analytical first and second derivatives. The availability of analytical second derivatives is essential for the efficient calculation of vibrational spectroscopy and, owing to the mathematical complexity, generating analytical second derivatives for the bond order based potentials represents a significant challenge. Furthermore, much of the complexity of the reactive potentials is not relevant for the calculation of vibrational frequencies, which are inherently an equilibrium property.

In this work we study the vibrational spectroscopy of carbon based materials using empirical potentials. The parameterisation of the well known potentials, such as the REBO potential [30], focuses on energetics and structure and does not consider the vibrational properties. As a consequence of this, it has been shown in a recent study that the REBO potential performed poorly in describing the vibrational frequencies of C₆₀ and CNTs [39]. It was found that to achieve an adequate description of the IR spectrum of C₇₀ and the RBM and G band of CNTs, it was necessary to treat high and low frequency modes separately. The calculation of vibrational frequencies has implications beyond simulating IR and Raman spectra. Vibrational frequencies provide an indirect probe of the potential energy surface, providing a measure of the curvature of the surface, and it is an open question as to whether empirical potentials which do not produce satisfactory agreement with experimental frequencies can provide accurate molecular dynamics.

Here we develop an empirical potential based upon the Murrell-Mottram (MM) potential that is designed to predict the vibrational frequencies of carbon based materials. Analytical first and second derivatives of the MM potential have been implemented and the potential reparameterised via a Monte-Carlo based hessian-matching approach. When combined with the empirical bond polarisation model [19] it provides a fully empirical method for modelling the Raman spectroscopy of CNTs and graphene. The implementation of analytical first and second derivatives allows accurate atomistic vibrational analysis and simulation of the Raman spectroscopy of systems with greater than 10,000 atoms. Subsequently, the Raman spectroscopy of graphene and CNTs with defects and junctions is explored.

2. Computational details

2.1. Parameterisation of the Murrell-Mottram potential

The work presented in this study is based upon the MM potential. This potential was chosen in preference to bond order potentials like REBO and Reaxff for its simplicity that allows for the implementation of analytical first and second derivatives and a more straightforward framework for parameterisation. For a system with N atoms, the MM potential [36] takes the following form with two and three body terms:

$$E = \sum_{i<j}^N V_{ij}^{(2)} + \sum_{i<j<k}^N V_{ijk}^{(3)} \quad (1)$$

where

$$V_{ij}^{(2)} = -D(1 + a_2\rho_{ij})\exp(-a_2\rho_{ij}) \quad (2)$$

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