Infrared-Active Modes in Finite and Infinite Hexagonal Boron Nitride

Oussama Boutahir¹, Souhail Lakhlifi¹, Mourad Boutahir*¹, Brahim Fakrach², Abdelhai Rahmani¹, Hassane Chadli¹, Abdelali Rahmani¹

¹Laboratoire d'Etude des Matériaux Avancés et Applications, Université Moulay Ismail, Faculté des Sciences Meknes, Morocco
²Laboratoire de Physique Théorique et Appliquée, Université Sidi Mohammed Ben Abdellah, Faculté des Sciences Dhar El Mahraz Fez, Morocco

*Corresponding author e-mail: mourad.boutahir@gmail.com

Abstract. In this theoretical paper, we study the Infrared spectra of h-BN as a function of their lengths. Calculations are performed in the framework of the force constants model, using the spectral moments method. This original approach allows us to consider not only infinite h-BN sheet as usual in most theoretical models but also h-BN sheet with finite lengths. These predictions are useful to interpret the experimental data.

1. Introduction
Hexagonal boron nitride (h-BN) is an interesting quasi two-dimensional insulator [1]. It has attracted intense scientific and engineering interest due to its excellent lubricity, high thermal, chemical stability and especially remarkable electronic properties. The band structure engineering of h-BN extends the exploitation of its potential applications.

Atomically thin two-dimensional (2D) materials [1,2] such as graphene, hexagonal boron nitride (BN), and the transition metal dichalcogenides (TMDCs) offer a variety of outstanding properties for fundamental studies and applications. More recently, the capability to assemble multiple 2D materials with complementary properties into layered heterogeneous structures presents an exciting new opportunity in materials design [2–8], but several fundamental challenges remain, including making good electrical contact to the encapsulated 2D layers. Electrically interfacing 3D metal electrodes to 2D surface is inherently problematic. For graphene devices, the customary approach is to metalize the 2D surface. In multilayer structures, the requirement to expose the surface for metallization presents additional restrictive demands on the fabrication process. For example, encapsulated BN/graphene/BN heterostructures (BN-G-BN) need to be assembled sequentially so as to leave the graphene surface accessible during metallization, because no process to selectively remove the BN layers has been identified. In this paper we focus on the infrared-active modes of BN sheet and BN nanoribbons

2. Model, Method & Approach:
The spectral moments method [9] was shown to be a powerful tool for determining vibrational spectra (infrared absorption, Raman scattering and inelastic neutron-scattering spectra) of harmonic systems.
This method can be applied to very large systems, whatever the type of atomic forces, the spatial dimension, and structure of the material.

For boron nitride intratube interactions of h-BN, we used the same force constant as used in recent calculations of the Infrared spectra of SWBNNTs [10]. The intensity of the infrared absorption spectrum is given by the following expression:

$$I_{\alpha}(\omega) = \frac{\omega}{nc} \sum_j \left| a_{j\alpha} \right|^2 \left( \delta(\omega - \omega_j) - \delta(\omega + \omega_j) \right)$$

(1)

With

$$a_{j\alpha} = \sum_k q_k \sqrt{m_k} e_j(k\alpha)$$

(2)

Where n and c are respectively the index of the material and speed of light, respectively, $\omega_j$ and $e_j(k\alpha)$ are respectively the frequency and the $(k\alpha)$ component of the displacement amplitude for the kth (\(\alpha\) is cartesian coordinate) in the jth mode. $q_k$ is the effective charge and $m_k$ is the mass of the kth atom. To enhance the IR response of nanotubes, dynamical effective charges on tied carbon atoms were fixed at $q_A=+1$ and $q_B=1$ for a given A-B bond. The usual method to calculate the IR spectrum consists of injecting in the previous expressions the values of $\omega_j$ and $e_j(k\alpha)$ obtained by direct diagonalization of the dynamical matrix of the system. However, when the system contains a large number of atoms, as for long dimer of SWNT, the dynamical matrix is very large and its diagonalization fails or require long computing time. By contrast, the spectral moment’s method [9] allows the Infrared spectrum of very large harmonic systems to be directly computed without any diagonalization of the dynamical matrix.

3. Results & Discussion:
In this section, we report the calculated infrared spectra for infinite BN sheet, which is obtained by applying periodic conditions. In order to identify all IR active-modes and their symmetries, we present in figure 1 the ZZ calculated Infrared spectra of BN sheet. Spectrum is displayed in the Intermediated wave-number (IWN) and high-wave-number (HWN) ranges.

![Figure 1. The ZZ polarized infrared spectra calculated for a h-BN sheet. Spectra are displayed in the Intermediated-like modes (ILM) and tangential-like modes (TLM) ranges.](image)
Concerning the intermediate-wave-number (IWN) region, from 600 to 1200 cm\(^{-1}\), the spectrum is dominated by a strong single mode located around 793 cm\(^{-1}\) of \(A_{1u}\) (A1) symmetry. This mode corresponds to an out-of-plane mode displacements of B and N atoms in the opposite directions, as illustrated in figure 2.

In the high-wave-number (HWN) range, above 1200 cm\(^{-1}\), the ZZ polarized spectra are dominated by strong IR-active modes. The ZZ spectra evidence that the Au mode is located at 1393 cm\(^{-1}\). The eigenvector displacements of this mode are given in figure 2, (the arrows indicate the magnitude and direction of B and N atom displacements). These vectors allow us to identify the longitudinal or transverse character of the optical modes. In the HWN range, all the modes are tangential modes.

![Figure 2. Infrared-active-mode atomic displacements and symmetries for selected normal modes in the h-BN sheet.](image)

The most important advantage of the spectral moment’s method is the possibility to calculate the infrared spectra for a finite and long width of BN nanoribbon. Now, we focus on Dependence of the width of nanoribbon. We calculated the ZZ infrared spectra of h-BN as a function of the width in the ILM (left) and TLM (right) see figure 3. Spectra are displayed for five finite widths, \(L = 2.15, 4.30, 8.61, 21.52, 86.10\) nm, and for infinite h-BN, from bottom to top.

From the figure 3 we show the ZZ polarized spectra of BN nanoribbon. We can see the existence of many active modes spread over two zones of the spectrum. Starting with the high wave-number region, one can clearly see the main mode detected around 1393 cm\(^{-1}\) that correspond to \(A_{1u}\) (A1) symmetry, and other new peaks appearing through edge effects. We next explore IWN region, also we can clearly see the main mode detected around 793 cm\(^{-1}\). Several other peaks are observed.
Figure 3. Dependence of the ZZ in the ILM (left) and TLM (right) infrared spectra of h-BN as a function of the length. Spectra are displayed for five finite lengths, $L = 2.15, 4.30, 8.61, 21.52, 86.10$ nm, and for infinite h-BN, from bottom to top.

In this paragraph, we have reported in figure 4 the calculated electronic band structures of h-BN monolayer. One can see that in the case of the monolayer, all spectral features remain essentially the same as for bulk h-BN, with the exception of the gap between the valence band (VB) and conduction band (CB), which has a significantly higher value (5 eV).

Figure 4. The calculated electronic band structures (left) and density of state (right) of h-BN monolayer.
4 Conclusion
In this work, we have calculated the Infrared spectra in the ILM and TLM ranges of h-BN, using the spectral moment’s method. The dependence of these modes has been calculated as a function of their chirality and lengths. The finite-size effects are shown to be significant only for short lengths, and the main effect of the length shortening is the appearance of additional peaks in the intermediate and tangential infrared domain.

References
[1] Xu M, Liang T, Shi M and Chen H 2013 Chem. Rev. 113 3766–98
[2] Geim A K, Grigorieva I V 2013 Nature. 499 419–425
[3] Mayorov A S et al 2011 Nano Lett. 11 2396–99
[4] Dean C R et al 2013 Nature 497 598–602
[5] Ponomarenko L A et al 2013 Nature. 497 594–597
[6] Georgiou T et al 2013 Nat. Nanotechnol. 8 100–103
[7] De Lillo F, Cecconi F, Lacorata and Vulpiani A 2008 EPL. 84 40005
[8] Topsakal M, Aktürk E and Ciraci S 2009 Phys. Rev. B. 79 115442
[9] Rahmani A, Sauvajol J L, Rols S and Benoit C 2002 Phys. Rev. B. 66 125404
[10] Fakrach B, Rahmani A, Chadli H, Sbai K and Bentaleb M 2012 Phys. Rev. B. 85 115437