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Understanding the lattice dynamics of multilayered h-BN: peculiar infrared optical responses

Luigi CigariniMichal Novotný, František Karlický
Department of Physics, Faculty of Science, University of Ostrava, Czech Republic.

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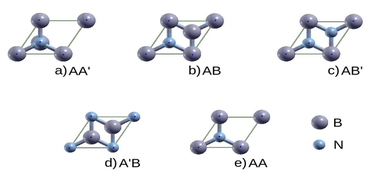
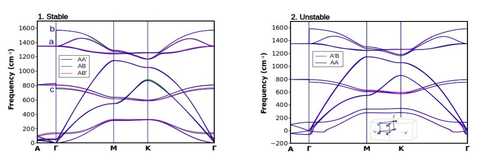
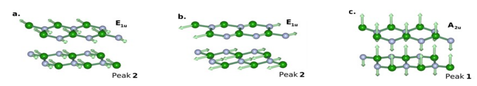
ABSTRACT

Stacking mismatches in hexagonal boron nitride (h-BN) nanostructures affect their photonic, mechanical and thermal properties and, to access information about the stacked configuration of layered ensembles, highly sophisticated techniques (like X-ray photoemission spectroscopy or electron microscopy) are necessary. Here, instead, taking advantage of the geometrical and chemical nature of h-BN, we show how simple models, based on shortened interplanar distances, can produce effective charge densities. Accounting these in the non-analytical part of the lattice dynamical description leads to a clarification of the experimental results from infrared spectroscopies and makes it possible to quantify the ratio of the differently stacked variants in the examined materials. These results come from the comparison of various density functionals and pseudopotential approximations (resulting to be particularly important in our study) in Density Functional Theory (DFT) and experimental data (from literature). Our model, therefore, proposes a semi-empirical method of discernment for h-BN stacking variants with the exclusive use of infrared spectroscopy.







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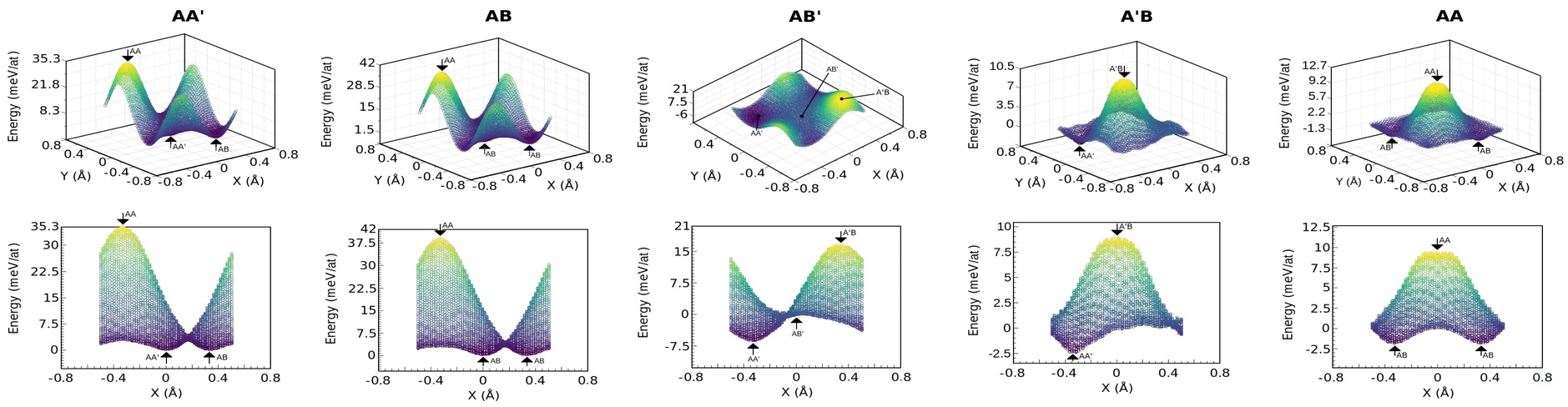
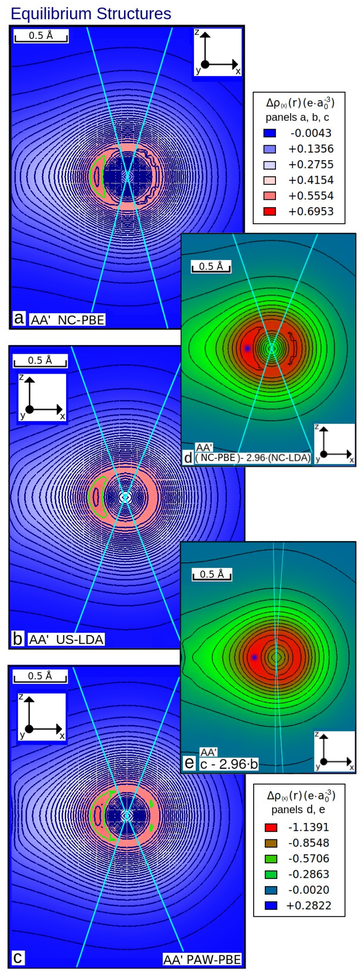
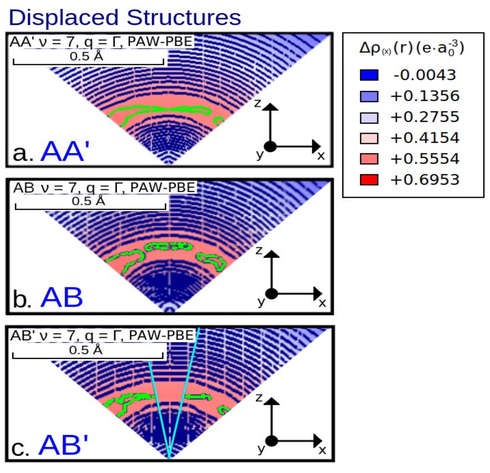
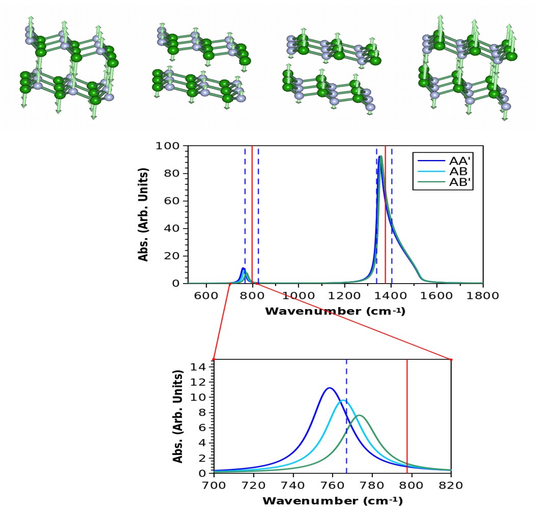
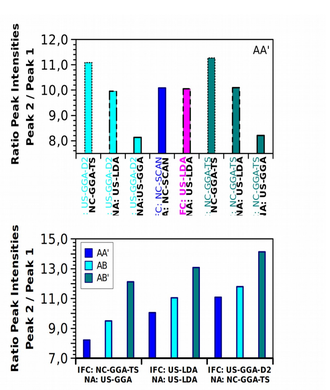
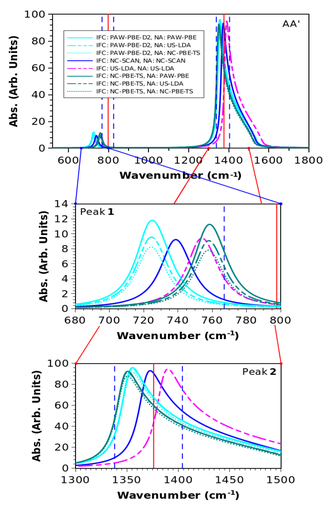




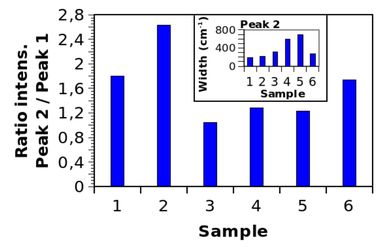


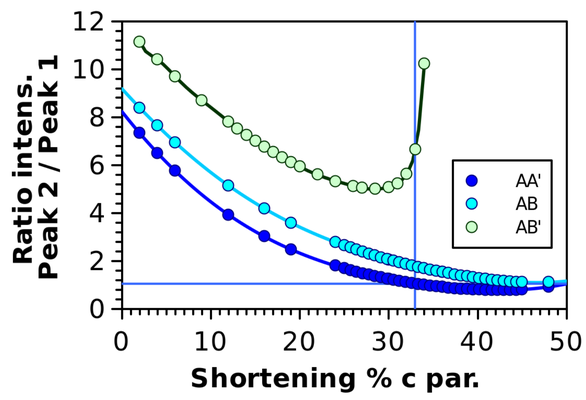


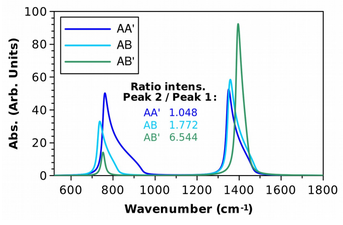




Experimental (from literature)







- Two distinct criteria of comparison with experiments: (1) the agreement between the calculated phononic frequencies (of selected vibrational modes, active in infrared or Raman spectroscopy) and the experimental counterparts and (2) the evaluation of the ratio between the intensities of the two IR active peaks.
- Comparison among theoretical methods: GGA, SCAN and LDA functionals, as well as NC, US and PAW pseudopotential approximations and different treatments of the van der Waals dispersion correction: a complex theoretical approach, based on GGA resolves the heterogeneous physics of the examined systems and produces a closer agreement with respect to the experimental numbers. FHI Troullier-Martins NC PP implementations produce a better agreement of the eigenvalues with respect to experimental measures, while Kresse-Joubert PAW PP deliver better performances in approaching the experimental order of magnitude regarding the ratios between IR absorption intensities.
- The analysis of the PES surfaces produced by parallel shifting of h-BN planes and lattice dynamical modes confirm the stability of the AA' and AB structures. Besides, a significant dynamical stability for the AB' symmetry point can be reasonably advanced.
- A dynamical stability of the AB' conformation, variable upon experimental conditions, produces a systematical presence, in different amounts, of this structured material in real samples. This conclusion theoretically explains the wide range of reported experimental values for the ratio between the two intensities of absorption in IR active peaks of h-BN. The results have been directly related to purely geometrical considerations, leading us to the proposal of a semi-empirical method for the calculation of the non-analytical part of the dynamical matrices (Born Q matrices and dielectric tensors) for this kind of systems.
- A significant amount of information about the h-BN stacking variability of multilayered real systems could be simply extracted by the exclusive use of infrared spectroscopy and vibrational analysis.

CONTACT PERSON

Luigi Cigarini

Department of Physics, Faculty of Science, University of Ostrava
luigi.cigarini@osu.cz

REFERENCES

[1]Li, Q. et al., Small, 12(1), 32-50 (2016).
[2]Yankowitz, M. et al., Nat. Rev. Phys., 1(2), 112-125 (2019).
[3]Henck, H., et al., Appl. Phys. Lett. 110.2 (2017): 023101.
[4]Jiang, P., et al., Phys. Rev. Mater. 2.6 (2018): 064005.
[5]Warner, J.H., et al., ACS nano 4.3 (2010): 1299-1304.
[6]Harrison, H., et al., Nanoscale Advances 1.5 (2019): 1693-1701.
[7]Ohba, N., et al., Phys. Rev. B 63.11 (2001): 115207.
[8]Cigarini, L., et al., arXiv preprint arXiv:2006.13168 (2020).

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