Vibrational Spectroscopy via Computer Simulations: Raman, Infra-Red and Related Methods

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Vibrational spectroscopies

Introduction

- We will run jobs on
  - Infra-red spectroscopy (CO_2 molecule, SiO_2 crystal)
  - Raman spectroscopy (Graphene nanoribbon)

Vibrational spectroscopies

Vibrational spectroscopies

Exercise: Graphene nanoribbons (GNR)

- We will study hydrogen-terminated, one-dimensional, infinitely long, armchair GNR (“GAR”)
  - Effect of width
  - Effect of termination
- Notes: Structures have been pre-relaxed in order to save computational time; dimensions of the cell (vacuum) have been minimised; convergence criteria have been tuned over the limits

Exercise: GNR

- We study the first GAR structure:
  - Investigate the structure using `XCrysDen`
  - First evaluate electronic structure:

    ```
    mpirun -np 4 pw.x -in gar-w_03-1H-pw.in > gar-w_03-1H-pw.out
    ```
  - Once finished, run

    ```
    mpirun -np 4 ph.x -in gar-w_03-1H-ph.in > gar-w_03-1H-ph.out
    ```

    This one will take more(!) time. If you are impatient, you can in the meantime proceed to the next slides
  - Once finished, run

    ```
    dynmat.x -in gar-w_03-1H-dynmat.in > gar-w_03-1H-dynmat.out
    ```
- After this you obtain the Raman spectrum with the command

  ```
  ./extract_spectra.scr gar-w_03-1H-dynmat.out
  ```

  in the file `gar-w_03-1H-dynmat-IR-br.dat`

Exercise: GNR

- Further GARs:
  - Investigate the structures in `gar-w_03-2H-pw.in`, `gar-w_04-1H-pw.in` and `gar-w_04-1H-pw.in` using `XCrysDen`; what is difference between the different ribbons?
  - To save time, we have already pre-calculated the dynamical matrix; all you need to execute is *eg*

    ```
    dynmat.x -in gar-w_03-2H-dynmat.in > gar-w_03-2H-dynmat.out
    ./extract_spectra.scr gar-w_03-2H-dynmat.out
    ```

    Then proceed as explained on the previous slide.

Exercise: GNR

- When you have the spectra from all the ribbons, plot the Raman spectra in files `gar-w_*-dynmat-Raman-br.dat` with a logarithmic scale on the vertical axis

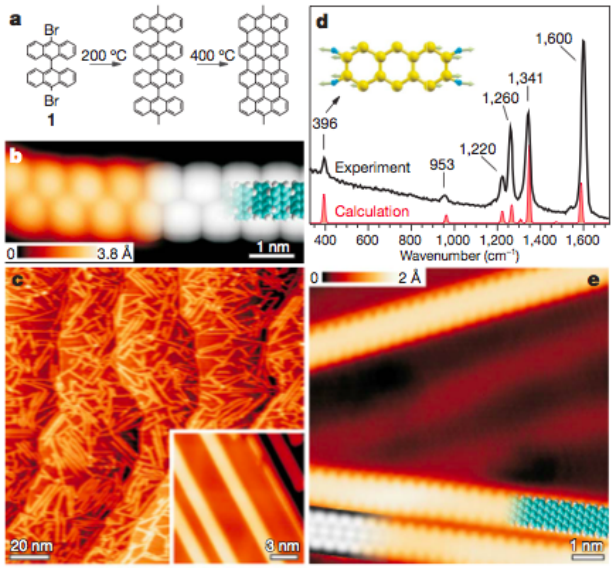
Physics: GNR

- Let us compare the structures with those in Paper `gnr1.pdf`
  - Find the notation used in the Paper for the edge terminations in our three structures
  - According to Figure 12 in the Paper, would our ribbons be metallic or semi-conducting? If the latter, what would be the band gap within DFT-GGA? (Hint: The narrowest ribbon in the Paper corresponds to the smallest possible ribbon)

Physics: GNR

- Let us compare the Raman spectra with that in Paper

`gnr2.pdf` :



- Can you find the mode corresponding to the one at 396 cm^{-1} in the file `gar-w_05-1H-dynmat.axsf` ?

Physics: GNR

- Let us now compare the dependency of the frequency of the breathing mode with the one found in Table II of Paper `gnr3.pdf`
  - Find the breathing mode in the files `gar-w_*-1H-dynmat.axsf`. Hint: It has the A_g symmetry. How does it change with the width of the GAR?

Thus this mode can be used to identify the width of the GARs (if they are present in large quantities).