# Supplementary Information to "Raman scattering of molecular graphenes" by M. Tommasini, C. Castiglioni, G. Zerbi

**Transformation of polarizability derivatives and treatment of redundancies**

Ring containing systems, such as those here investigated, are known to possess set of redundant internal coordinates. In particular, for Polycyclic Aromatic Hydrocarbons and graphite, CC stretchings and in-plane angle deformations (bendings) appear mixed in redundancies [Mapelli]. For this reason, transformations of molecular properties between cartesian and internal coordinates systems require some care. In the following sections we describe the procedures we have followed for dealing with polarizability derivatives obtained with the Hückel approach and DFT calculations. It is worth recalling that polarizability derivatives are naturally obtained with respect to cartesian nuclear displacements in DFT calculations and with respect to CC stretching coordinates in the Hückel model.

Procedure **(1)** has been used to calculate Raman intensities from polarizability derivatives obtained with the Hückel model and normal modes obtained from DFT dynamics expressed in cartesian coordinates. Procedure **(2)** has been used to transform DFT polarizability derivatives from cartesian nuclear displacements to valence internal coordinates.

**(1)** Within the Hückel-based approach to the calculation of polarizability derivatives, redundancies are simply avoided because one considers just the (non redundant) set of CC stretching coordinates (polarizability derivatives along non CC stretching internal coordinates have been neglected in this model). Since vibrational dynamics is available from DFT in cartesian coordinates, to obtain Hückel-based Raman intensities it is necessary to convert the polarizability derivatives along CC stretching coordinates (**R**) into polarizability derivatives along cartesian coordinates (**x**) by using Wilson's **B** matrix [Wilson].

We recall that the **B** matrix establishes the linear transformation between internal and cartesian coordinates (in the following, the sum over repeated indexes is implied):

$$R_i = B_{ik} x_k \qquad [1]$$

Based on Eq. [1], one can write, for the polarizability derivatives (α stands for a generic component of the polarizability tensor):

$$\frac{\partial \alpha}{\partial x_k} = \frac{\partial \alpha}{\partial R_i} \frac{\partial R_i}{\partial x_k} = \frac{\partial \alpha}{\partial R_i} B_{ik} \qquad [2]$$

Eq. [2] allows to easily compute polarizability derivatives along cartesian coordinates once are known the polarizability derivatives along internal coordinates (in our case just CC stretchings).

By numerically solving the vibrational dynamics in cartesian coordinates (being known the force field from DFT calculations) one gets the normal coordinates (**Q**), and nuclear displacements (**L**) which are related to the cartesian displacements (**x**) according to [Wilson]:

$$x_i = L_{ik} Q_k \qquad [3]$$

This linear relationship allows to quickly obtain the polarizability derivatives along the normal coordinates:

$$\frac{\partial \alpha}{\partial Q_k} = \frac{\partial \alpha}{\partial x_i} \frac{\partial x_i}{\partial Q_k} = \frac{\partial \alpha}{\partial x_i} L_{ik} \qquad [4]$$

From the polarizability derivatives along normal coordinates given by Eq. [4], Raman intensities can be obtained straightforwardly [Wilson].

**(2)** Redundancies have to be considered when comparing DFT polarizability derivatives with polarizability derivatives obtained with the Hückel method (data reported in Figure 3). The required transformation of DFT polarizability derivatives along cartesian nuclear displacements coordinates into polarizability derivatives along CC stretching coordinates is carried out by using a full set of redundant in-plane internal coordinates (i.e. all CC and CH stretchings, all in-plane bendings) defined according to [Wilson]. This is necessary because one has to invert Eq. [2] which requires to compute the inverse of the rectangular **B** matrix (i.e. the **A** matrix [Wilson]). The **A** matrix can be obtained if the set of internal coordinates correctly span the vibrational space (in particular, at least the subspace of in-plane vibrations for the planar molecules here considered). The set of only CC stretching coordinates is not enough for this task, unless in-plane bendings are added.

The **A** matrix is computed through the inverse of the **G** matrix [Wilson], which in presence of redundancies is singular (the zero-valued eigenvalues of **G** are associated to redundancies [Gussoni]). Therefore, the inversion of **G** has to be carried out carefully, by working in the subspace spanned by the eigenvectors associated to the non-zero eigenvalues of **G**, as described in [Gussoni]. In this way redundancies are projected out and polarizability derivatives along CC stretching coordinates can be obtained from cartesian derivatives computed with DFT methods. The procedure just described has been followed to obtain the data reported in Figure 3.

# References

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