

DFT simulations of the Raman response of sp carbon-atom wires: from electron-phonon coupling to charge transfer effects

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Carbon-atom wires (CAWs) are linear, finite-length molecules, whose ideal limit is the so-called “carbyne”, the 1D carbon allotrope with outstanding theoretical properties [1,2]. In the last years, CAWs became an interesting subject in nanoscience and nanotechnology for their peculiar electronic and vibrational structure, which determines their optical and transport properties. Indeed, similarly to other carbon-based polyconjugated systems, CAWs can be affected by a variety of intramolecular (by means of chemical functionalization/selection of end-groups) and intermolecular interactions that can modulate their insulating–semiconducting–metallic behavior. Two classes of CAWs can be identified: polyynes (bond-length-alternated chains with insulating/semiconducting character), and cumulenes (more equalized systems with nearly metallic behavior).

A fundamental issue regards how and to what extent the properties of CAWs can be modulated by controlling π -electron conjugation. In this context, Raman spectroscopy proved to be a useful probe [3], as it is for many other nanostructured carbon materials.

In this contribution, we present an overview on the use of Density Functional Theory calculations to predict the Raman response of CAWs and to provide an interpretation of their physico-chemical properties. These studies have been carried out in the framework of the Effective Conjugation Coordinate model (ECC) [4], developed and widely employed for polyconjugated materials.

First, DFT-computed phonon dispersion curves of carbyne are discussed to highlight the role of electron-phonon coupling and of π -electron confinement in modulating the vibrational and the electronic properties, establishing a correlation between the properties of the ideally infinite 1D chain and those of finite size molecules. The investigation is supported also by the development of suitable tight-binding models.

Focusing then on finite-length molecules, most of which have been characterized experimentally, we explore how intramolecular interactions in CAWs can be modulated by a proper choice of end-groups, switching from a polyyne-like to cumulene-like behavior. The interpretation of the Raman spectra of these systems is carried out by computing also the electronic gap and the values of bond length alternation (BLA), to highlight the mutual dependencies among all these properties. We discuss in detail the effects of end-groups constituted by different aromatic groups of increasing size, cumulene-inducing terminations and donor-acceptor moieties.

Finally, the occurrence of charge transfer between CAWs and metal nanoparticles is discussed by analyzing Surface Enhanced Raman Spectra (SERS) of selected systems and interpreting them based on DFT calculations. Molecular simulations demonstrate that the structure and the electronic properties of CAWs can be widely modulated either by controlling the amount/direction of charge transfer or by the choice of the end-groups; moreover, these effects can be monitored by a detailed analysis of their Raman spectra [5].

The results here presented provide guidelines for the design of novel nanostructures based on CAWs, including both sp-sp² hybrid systems where graphene-like and polyyne-like domains are closely interconnected, or donor/acceptor systems including heteroatoms. The capability to tune the final electronic or optical response of the material makes indeed all these systems very appealing for a future carbon-based science and technology.

Moreover, we further demonstrate that Raman spectroscopy proves to be a very important characterization technique to unveil the connections between structural, vibrational and electronic properties of conjugated sp-carbon systems, going well beyond its application as a simple analytical method.

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