

# Structure and Raman scattering of chained carbon films on copper substrate: ab initio approach

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**Abstract.** During the past decades one-dimensional carbon allotropes were attracting much interest. One of such modifications consists of the  $sp^1$  chains, ordered in a hexagonal array with nearly 5 angstroms interchain spacing – linear-chained carbon (LCC). The technological problem of LCC synthesis is the lack of characterization technique confirming its structure along chains. In this work we try to improve the simple structural model of LCC by adding copper substrate and dopants. We compare the experimental Raman spectra with ones modelled by DFT. The calculation results explain the low-frequency features seen in experimental Raman spectra by the substrate-enhanced interaction of carbon chains.

## 1. Introduction

A plenty of carbon nanomaterials have been studied in the last few decades [1, 2]. They already have a large variety of applications in daily life and industry. In 1985 the discovery of  $C_{60}$  molecules made major contribution to medical applications [1]. Another type of carbon material, carbon nanotubes, was proven to give impressive elastic moduli [2]. More recently discovered carbyne [2] is predicted to be a strong material as well [3]. Theoretical study of Young's modulus of carbyne, a parallel carbon chains with kinks, gives a breakthrough at over 1TPa which attracts material scientists [3, 4]. Other unique properties of carbyne and its modifications, such as linear-chained carbon (LCC), provide wide application areas ranging from nanoelectronics to medicine.

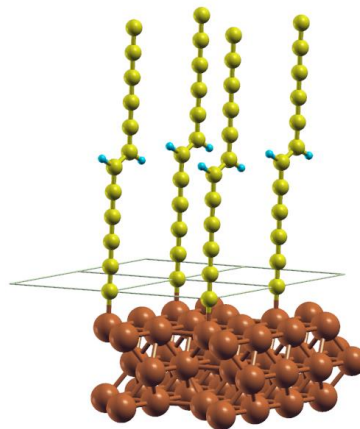
Though a pure carbyne crystal of macroscopic size has never been synthesized, the LCC films with 5 angstrom chain-to-chain distance have been produced since 1990s [5]. One of the problems that arise in the synthesis of LCC is the lack of rapid characterization technology, which confirms the structure of the new material. At the same time, the Raman scattering method is able to detect carbon chains and reflects their structural features [6]. The shape of the Raman spectrum of LCC films differs significantly from that of isolated carbon chains [7] due to the Coulomb and Van der Waals interaction of chains in the array. The lines in the spectrum are largely broadened, their interpretation is difficult and cannot be performed within the framework of a simple structural model like one proposed by M.B. Guseva and V.G. Babayev [5]. The reason may be in the model factors not taken into account: the effect of the substrate, impurity atoms, and the degree of structural disorder.

The purpose of this paper is to modify the structural model of a LCC film on a copper substrate (see figure 1) with further comparison of the experimental and calculated Raman spectra.



## 2. Numerical techniques

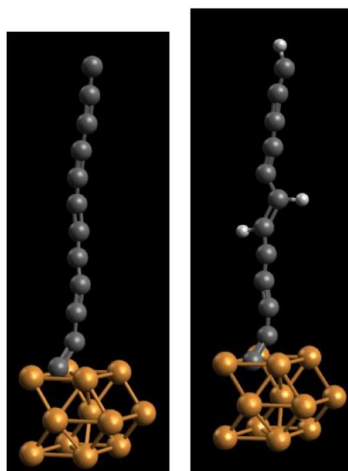
The modified structural model used in this paper (2D surface slab, see figure 1) includes three near-surface atomic copper layers and a chain of 12 carbon atoms with a kink. The impurity atoms were placed on the kinks and ends of the chains. The interatomic distances were: C-C 1.275 Å, C-H 1.09 Å, Cu-C 1.86 Å. To calculate the structure, phonon modes and the intensity of the corresponding Raman lines of carbon chains on the crystalline copper substrate (111) and (001) (figure 1), the density functional theory (DFT) method was used with the use of the relativistic LDA pseudopotential HGH [8] and a cutoff energy of 45 Ha in the ABINIT package [9]. SCF convergence was achieved with  $10^{-12}$  Ha tolerance for absolute differences of total energy. Substrate atoms were fixed, positions of carbon and impurity atoms were relaxed by Broyden-Fletcher-Goldfarb-Shanno minimization down to a maximal absolute force tolerance of  $5 \cdot 10^{-6}$  Ha/Bohr. We used the dispersion correction method vdW-DF2 (LMKLL) [10]. Integration over the Brillouin zone was carried out using  $7 \times 7 \times 1$  Monkhorst and Pack grids [11].



**Figure 1.** Schematic diagram of the LCC structural model on a copper substrate used for ab initio calculations.

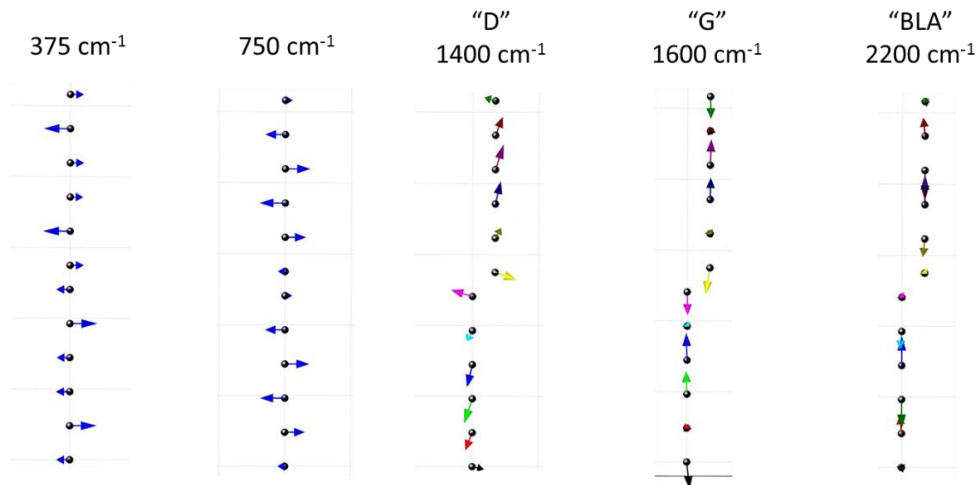
## 3. Results and discussion

The results of structural optimization with the minimization of the total energy (figure 2, left) show that, in the absence of impurities, the chain on the copper surface straightens, the kinks disappear. Hydrogen atoms provide a bending angle close to 45 degrees (figure 2, right).

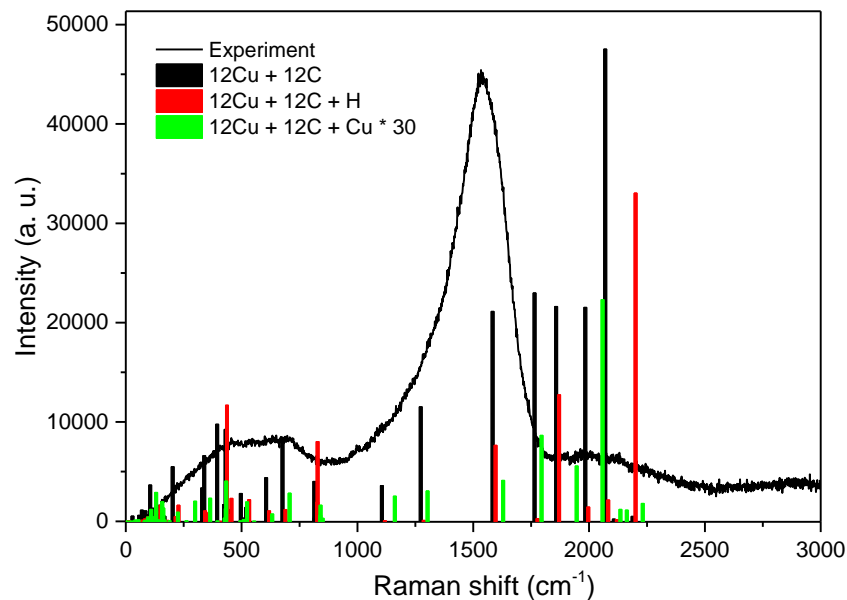


**Figure 2.** Structural relaxation results for carbon chains on copper substrate.

DFT modelling of the crystal of carbon chains with 6 atoms straight section and 60 degree kink allows to identify the types of normal vibration modes involved into the Raman scattering. The corresponding eigenvectors are shown in figure 3. One can see that the low-frequency modes ( $375\text{ cm}^{-1}$  and  $750\text{ cm}^{-1}$ ) correspond to the chain bending. The so-called D and G modes are common for the Raman spectra of different carbon allotropes. In our case the D mode corresponds to the atoms displacements away from chain axis, while G and BLA (bond length alternation) vibrations occur along this axis.



**Figure 3.** Eigenvectors of the Raman-active vibrational modes of kinked carbon chains. Kinks are not observable for the first two chains due to view angle rotation.



**Figure 4.** Comparison of the experimental and calculated spectra of carbon chains on the copper surface (111). The Raman intensity for copper-doped chains is multiplied by a factor of 30.

The calculated Raman spectra of LCC structures on a copper substrate are shown in figure 4: pure, hydrogen- and copper-doped chains on Cu(111) plane. For comparison, the experimental spectrum of the LCC film on a polycrystalline copper substrate is presented at the background [7]. Compared with

the previous model of linear-chain carbon, they better describe the transverse vibrations of the chains ( $500\text{--}1300\text{ cm}^{-1}$ ), and the longitudinal ones are worse.

The copper impurity reduces the intensity of the Raman spectra by a factor of 30. A small number of bends, and therefore  $\text{sp}^2$ -bonds, in comparison with the bulk LCC crystal, reduces the intensity of the  $1500\text{ cm}^{-1}$  peak and unnecessarily increases the maxima in the  $2000\text{ cm}^{-1}$  region.

The presence of hydrogen leads to a shift in the lines in the Raman spectrum to the high-frequency region. The admixture of copper sharply reduces the intensity of the Raman scattering by damping the vibrations in the region of the bends.

Appearance of calculated Raman lines in the range of  $550\text{--}900\text{ cm}^{-1}$  may be explained by the substrate-enhanced interaction between chains in LCC/Cu structure. This mechanical coupling is combined with weak Van-der-Waals forces, which induces low-frequency modes at tenths of  $\text{cm}^{-1}$ . Further improvement of the model is desirable in order to approximate well the whole experimental spectrum. One may take into account not only electronic, but also magnetic properties of the system. However the general interpretation of the Raman bands is now provided by a combination of simple infinite 3D LCC model [7] and a 2D surface slab model described in current work.

#### 4. Conclusion

In this paper, the Raman spectra of linear-chained carbon have been studied numerically. A modified structural model of LCC with hydrogen and copper impurities on a copper substrate is proposed. Impurity atoms provide the existence of kink of carbon chains.

The copper substrate provides additional interaction between the chains, which enhances the amplitude of their transverse oscillations, bringing the results of the calculation closer to the experimental data.

The small number of kinks and, consequently  $\text{sp}^2$ -bonds, compared with the bulk crystal, reduces the intensity of the peak  $1500\text{ cm}^{-1}$  and unnecessarily increases the maxima in the vicinity of  $2000\text{ cm}^{-1}$ .

The presence of hydrogen leads to a shift in the lines in the Raman spectrum to the high-frequency region. The admixture of copper suddenly reduces the intensity of the Raman scattering by damping the vibrations in the region of the kinks.

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