



# Nonlinear atomic vibrations and structural phase transitions in strained carbon chains



G.M. Chechin\*, D.A. Sizintsev, O.A. Usoltsev

Southern Federal University, Zorge 5, Rostov-on-Don, Russian Federation

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## ABSTRACT

We consider longitudinal nonlinear atomic vibrations in uniformly strained carbon chains with the cumulene structure ( $=C=C=$ )<sub>n</sub>. With the aid of *ab initio* simulations, based on the density functional theory, we reveal the phenomenon of  $\pi$ -mode softening in certain range of its amplitude for the strain above the critical value  $\eta_c \approx 11\%$ . Condensation of this soft mode induces the Peierls phase transition connected with doubling of the unit cell. We introduce a simple classical model without any adjustable parameters that allows one to describe quite well the properties of the  $\pi$ -mode softening. Besides the  $\pi$ -mode, two other symmetry-determined nonlinear normal modes can exist in monoatomic chains with arbitrary interparticle interactions. They correspond to tripling or quadrupling of the vibrational unit cell. Softening of these modes allows one to suppose that two new types of carbon chains (besides cumulene and polyynes) can exist with bond lengths alternation different from that of polyynes. Since the phase transitions in the strained cumulene can significantly change its electronic properties, these phenomena can be used for constructing various nanodevices.

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## 1. Introduction

Monoatomic carbon chains can exist in two different modifications. The first one is polyynes, or carbyne- $\alpha$ , representing the chain with alternating single and triple bonds [chemical structure  $(-C \equiv C-)_n$ ]. The second modification is cumulene, or carbyne- $\beta$ , representing the chain with double bonds [chemical structure  $(=C=C=)_n$ ]. Despite the fact that carbyne was discovered by a Russian chemist A.M. Sladkov in 1971 [1], intensive study of this unique material started fairly recently. Carbyne chains were claimed to be the strongest material known at the present time. Synthesis of linear carbon chains up to 6000 atoms in carbon nanotubes was reported in [2]. Because of many unique mechanical, physical, and chemical properties, which were experimentally studied or theoretically predicted, carbyne is considered as perspective material for various nanodevices, for hydrogen storage, etc. (see [2–7] and papers cited therein). We would like to emphasize that a substantial interest exists not only in individual carbyne chains, but also in the so called oriented carbyne, which represents an array of parallel carbon chains. Many interesting properties of this material were reported in the experimental papers [8–12]. In

particular, it was revealed that oriented carbyne is a topological insulator and that it can demonstrate giant pseudo-magnetic field, which, in turn, induces Landau quantization of the energy levels of charge carriers.

Chemical synthesis of pure carbyne chains and their experimental study are very difficult and, therefore, theoretical *ab initio* investigations, in particular those based on the density functional theory (DFT), play a rather important role in prediction of its properties and in description of different physical phenomena, which are possible in this material. Many interesting results on strained carbyne chains were obtained with DFT computer simulations. In the paper [7], DFT *ab initio* methods allow to reveal that distribution of bond lengths and magnetic moments at atomic sites exhibit even-odd disparity depending on the number of carbon atoms in the chain and on the type of saturation of these atoms at both ends. It was also found that local perturbation created by a small displacement of the single carbon atom at the center of a long chain induces oscillations of atomic forces and charge density, which are carried to long distances over the chain. Systematic investigation of structural and mechanical properties of strained carbon chains with  $N < 22$  atoms was presented in [13], as well as in [7], where it was found that these properties essentially depend on the parity of the number  $N$ . In particular, the interatomic distances (bond lengths) near the chain edges turn out to be different

\* Corresponding author.

E-mail address: [gchechin@gmail.com](mailto:gchechin@gmail.com) (G.M. Chechin).

URL: <http://www.sfedu.ru> (G.M. Chechin).

for chains with odd or even  $N$  and, as a consequence, the former are stronger than the chains with even  $N$ .

In the paper [3], structural transformation of cumulene under certain strain was revealed. This is the Peierls phase transition, which leads to the radical change of carbyne electron spectrum. As a result of this transition, an energy gap in the electron spectrum appears and the conductive cumulene transforms into poly-yne which is semiconductor or insulator. This phenomenon opens perspectives to control electrical behavior of carbyne by mechanical strain [3].

All of the aforementioned papers, devoted to DFT-studying of properties of strained carbyne, deal actually with a static structure of this material.<sup>1</sup> In contrast, the problem of nonlinear atomic vibrations in strained carbon chains was studied for the first time in our paper [14]. During this study we revealed an unexpected phenomenon of softening of the longitudinal  $\pi$ -mode vibrations above a certain critical value of the strain. Some results of this study were published in the brief paper [14]. They can be summarized as follows.<sup>2</sup>

For strains lower than  $\eta = 11\%$  cumulene demonstrates monotonic *hard* type of nonlinearity (the frequency grows with increase of the  $\pi$ -mode amplitude  $a$ ). However, for  $\eta > 11\%$  there is a certain range of amplitudes  $a$  in which *soft* nonlinearity occurs, namely, the frequency of the  $\pi$ -mode abruptly *decreases* and then again begins to increase.

The phenomenon of vibrational modes softening is well known in the theory of structural phase transitions [15] where by condensation (“freezing”) of such modes one tries to explain the nature of the displacement-type phase transitions. This is the so-called concept of *soft modes*. It is essential that in the majority of the papers on this subject, soft modes are treated in purely phenomenological manner with some vague arguments about the change of electron-phonon interactions in crystal under change of such external parameters as temperature and pressure. In contrast to these works, in our study a soft vibrational mode in cumulene appears as a direct result of the *ab initio* simulation *without* any additional assumptions.

In [14], the phenomenon of the  $\pi$ -mode softening has been explained by the fact that above the critical value of the strain the old atomic equilibrium positions (EQPs) become unstable and two new EQPs appear near each of them. Namely, vibrations in the vicinity of these new EQPs correspond to the softening of the  $\pi$ -mode. In turn, condensation of the  $\pi$ -mode leads to a new atomic equilibrium configuration that corresponds to the Peierls phase transition. After this transition, the unit cell turns out to be twice as large than that of cumulene, and the carbon chain transforms into another carbyne form, poly-yne, with bond lengths alternation.

The main *ab initio* results obtained in our work and in the paper [3] are sufficiently close to each other. Some discrepancy can be explained by different approximations used in the framework of DFT approach (different exchange–correlation functionals, different sets of basis functions for solving Kohn–Sham equations, different realization of the numerical methods in the packages ABINIT and VASP, etc.). Nevertheless, our results and those from [3] are identical qualitatively (detailed comparison will be presented elsewhere).

Our work is purely theoretical. However, we think that the obtained results may be used in construction of new nanotechnology devices, in which electrical properties of carbyne can be controlled by mechanical strain. The presented results can also be

useful for searching new forms of carbyne, which are predicted in this work.

In the present paper, we discuss not only the condensation of the  $\pi$ -mode, which was already considered in previous brief paper [14], but also condensation of two other symmetry-determined nonlinear normal modes (NNM), which are possible in cumulene chains. With the aid of our approach combined with some group-theoretical methods [16], we predict the possibility of existence of two new types of carbon chains, besides cumulene and poly-yne. They both possess alternation of bond lengths, but with *different alternating schemes* compared to that of the poly-yne.

It is worth mentioning a specific direction of research related to the study of mechanical properties of carbyne and other carbon nanostructures within the framework of the theory of continuous media elasticity. For example, in [4], the following issue is discussed: “The chain of carbon atoms is a nanorod, or a nanorope?”

In [17–20], mechanical properties of carbon nanotubes of various types and nanobeams are studied within the framework of the theory of a continuous elastic medium with nonlocal interactions. On the other hand, as was already mentioned, the long chains of carbyne were synthesized inside carbon nanotubes. Taking into account this circumstance, one can hope that methods and results obtained within the framework of the theory of continuous medium elasticity could be useful, to some extent, in studying the mechanical properties of such complex systems as nanotubes with carbyne chains.

The paper is organized as follows. In Section 2, we consider the  $\pi$ -mode atomic vibrations in the strained cumulene in the framework of the DFT model and discuss the properties of these vibrations near new EQPs. The simple model of the monoatomic chain whose particles interact via the Lennard–Jones potential (L–J chain) is introduced in Section 3 and the appearance of the new EQPs is explained. In Section 4, we discuss the stability of these equilibrium positions. In Section 5, the notion of the symmetry-determined Rosenberg NNMs in monoatomic chains is considered. In Section 6, we discuss the properties of these modes in the framework of the L–J model and results of their condensation in the cumulene chains. Some computational details are given in Section 7, while Section 8 contains conclusion remarks on nonlinear dynamics of the strained carbon chains.

## 2. $\pi$ -mode vibrations within the DFT model

We investigate *longitudinal* atomic vibrations of *uniformly strained* carbon chains in the  $\pi$ -mode dynamical regime. This strain is modeled by an artificial increase of the unit cell size ( $R$ ) with respect to that of the chain without strain ( $R_0$ ). Thus, speaking about the strain of the chain by  $\eta$  per cent, we mean that  $R = R_0(1 + \eta)$ .

The set of atomic displacements  $\mathbf{X}(t) = [x_1(t), x_2(t) \dots x_N(t)]$  of the  $N$ -particle carbon chain for such vibrational regime at a fixed time  $t = t_0$  can be written as follows:

$$\mathbf{X}(t_0) = [a(t_0), -a(t_0)|a(t_0), -a(t_0)| \dots | a(t_0), -a(t_0)]. \quad (1)$$

In this pattern, all  $x_i(t)$  with odd numbers are equal to  $a(t_0)$ , while those with even numbers are equal to  $-a(t_0)$ . Thus, all neighboring atoms vibrate out of phase with equal amplitudes. The unit cell for describing  $\pi$ -mode vibrations of the chain with periodic boundary conditions is twice larger than that of the equilibrium state. Since two carbon atoms in this unit cell possess, at any time  $t$ , displacements  $x(t)$  and  $-x(t)$ , one can discuss the time evolution of only one of them choosing the origin at its equilibrium position. To excite the  $\pi$ -mode vibrations in the chain we assume  $x(0) = a, \dot{x}(0) = 0$ .

<sup>1</sup> Linear vibrations (phonon spectrum) of strained carbyne were partially discussed in [4].

<sup>2</sup> Unfortunately, we were not aware of the paper [3] when prepared our own paper [14].

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