



Research paper

Chains of benzenes with lithium-atom adsorption: Vibrations and spontaneous symmetry breaking

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ABSTRACT

We study effects of different configurations of adsorbates on the vibrational modes as well as symmetries of polyacenes and poly-*p*-phenylenes focusing on lithium atom adsorption. We found that the spectra of the vibrational modes distinguish the different configurations. For more regular adsorption schemes the lowest states are bending and torsion modes of the skeleton, which are essentially followed by the adsorbate. On poly-*p*-phenylenes we found that lithium adsorption reduces and often eliminates the torsion between rings thus increasing symmetry. There is spontaneous symmetry breaking in poly-*p*-phenylenes due to double adsorption of lithium atoms on alternating rings.

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1. Introduction

Adsorption of lithium atoms and other alkali metals to conjugated carbon systems has shown the possibility of strong deformations which may occur as spontaneous symmetry breaking [1–5]. Polyacenes have served as paradigmatic examples [1,2,5] but similar effects have previously been discussed in other aromatic molecules [3,5]. The question as to what extent such adsorption can be detected leads to a comparison between the vibrational spectra of the corresponding molecules. One focus here is on polyacenes, in particular on anthracene for two reasons: First, it is in this context that interesting near-periodic structures are seen which are relevant to narrow graphenic nano-ribbons [4]; Second, the matter of spontaneous symmetry breaking is quite clear in these structures, as we shall see. Further, another type of benzenoid species is studied, namely the poly-*p*-phenylenes (PPP) we find that adsorption here increases certain (distortive) similarities to polyacenes, in that torsion present in the naked PPP is suppressed. Notably PPPs are less chemically reactive (and so much easier to handle) as compared to polyacenes. Also their potential for branching allows a richer spectrum of future extension of the present work.

The question arises as to how such deformations affect the stiffness of the molecules and to what extent low-lying modes couple movements of the underlying chains and movements of adsorbates. We study Li adsorption, manifesting interesting effects:

spontaneous symmetry breaking and fairly large charge transfers. The extension to linear PPPs is very suggestive because they represent the narrowest “armchair” graphene boundary [6,7]. One great difference is that (neutral) PPPs are not flat and thus seem to be far from armchair edge nano-strips but interestingly we find that they flatten when subject to adsorption of lithium atoms.

We use DFT calculations to obtain the pertinent data from which we obtain the structure and further data that determine the vibrational modes. We then proceed to calculate the vibrational modes. Next we discuss the differences in the spectra and observe that with few exceptions the actual dynamics of low lying frequencies is much the same as that of the underlying spectrum of the simple (naked) polyacenes. The purpose is to show how things change with heavier and larger adsorbates.

The need to analyze vibrational modes of such systems naturally arises to enhance structural understanding. On one hand we would like to know if the spectra are sufficiently different to allow the identification of a given configuration and on the other hand, whether the structure of low lying modes indicates some decoupling of the movement of the naked molecule (skeleton) from the movement of the adsorbates. If indeed such a decoupling happens it would be important to know which modes are lower. We present this analysis in some detail for the case of anthracene, to find that the spectra are quite different; furthermore we find the usual scenario, the first few modes are vibrations of the skeleton which are essentially followed by the adsorbates, though exceptions occur. These results will lead us to a speculative discussion of the possibility to use such chains, most likely PPP's, with regularly spaced

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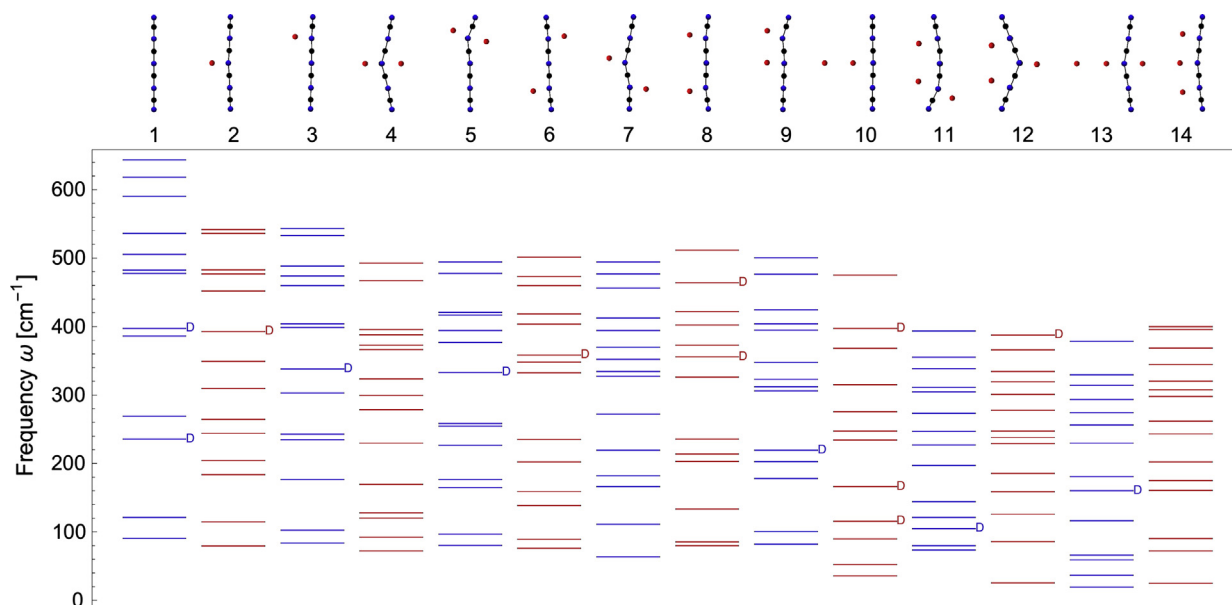


Fig. 1. Vibrational spectra of anthracene and anthracene with Li adsorption. In this figure and in all following vibrational spectra, 15 modes are shown for each molecule. Tight doublets are indicated by the letter D to make sure that they can be identified.

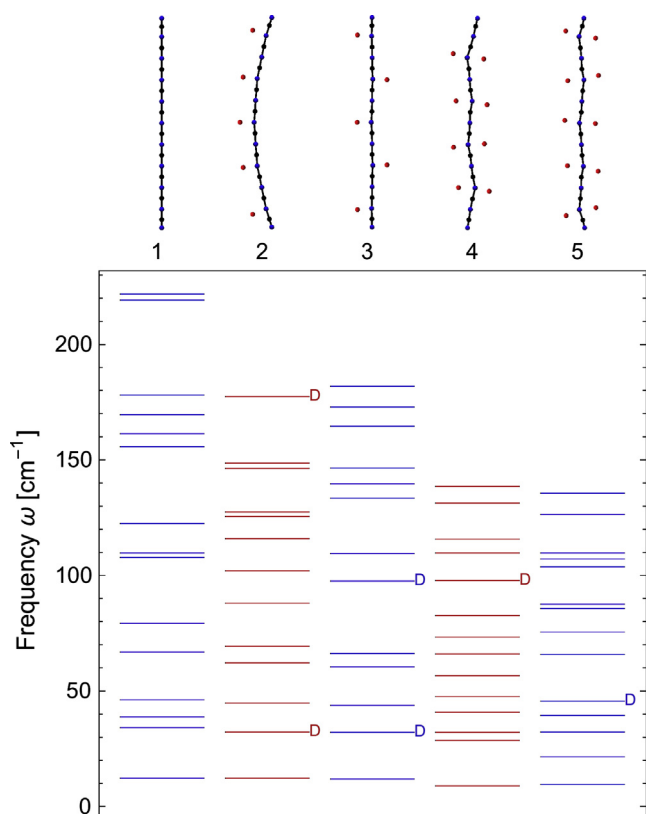


Fig. 2. Vibrational spectra for nonacene and for some configurations of nonacene under Li adsorption.

adsorbates as substrate for quantum register using the adsorbates as the string of qubits and the vibrations as extended qubits to mediate the information for control gates in the spirit of the Innsbruck quantum computer [8,9]. There an ion chain in a quasi 1-D trap serves as qubit chain and the collective motion of the ions to mediate information for control gates. We will not discuss the quantum optical necessities to implement such a scheme coupling

the ions by molecular vibrations and the qubits by adsorbed Li atoms. Rather we simply point out that a possibly viable structure exists. In particular we present some configurations of polyacenes and PPP's that fulfill the obvious criteria we need: Low lying largely decoupled modes of movement of the skeleton.

For PPPs torsion modes will also appear in the lower part of the spectra, and they similarly tend to decouple at low frequency from the other modes, this has been seen in other carbon systems [10]. Again there are exceptions. Nevertheless, the prevailing feature of decoupling of modes for the lowest states is interesting and may be relevant in various aspects not presently obvious.

We proceed as follows: First we discuss briefly the computational methods used. We then proceed to discuss anthracene in detail analyzing 14 configurations with zero up to four lithium atoms adsorbed. Some aspects relating to spontaneous symmetry breaking in infinite systems and their relation to the Peierls transition are commented as supplement. Finally we give some conclusions and an outlook.

2. Computational methods

The calculations for individual molecules were performed with the GAUSSIAN09 program codes [11]. Geometry optimizations were made with DFT [12] using hybrid functional B3LYP [13]. We have selected the 6-311g [14] basis sets for electronic structure calculations that use linear combinations of gaussian functions to form the orbitals. Additionally, we use the improvement of these basis sets by adding d functions to carbon atoms.

To test whether polarization is important we rerun some of the calculations with two different basis sets that include such terms, 6-31g+(d) and 6-311++g(d,p). Also we used alternatively the functionals MPW1PW91 [15–17] and B3PW91 [13,15,18]. Those functionals have been used in carbon systems [19,20] as well as in alkaline molecules [21] which have been reported to yield very accurate vibrational frequencies and IR intensities. No qualitative difference could be seen in the results, both for the structure and the vibrational spectra, therefore we do not show the corresponding figures.

The frequency calculations were made with the same package, by determining the second derivatives of the energy with respect

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