

Long range vibrational interactions in linear carbon chains

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Abstract

Le catene lineari di carbonio sono sistemi coniugati particolarmente interessanti dal punto di vista elettronico e vibrazionale per la presenza di interazioni a lungo raggio causate dalla delocalizzazione degli elettroni π . In questo articolo il campo di forze vibrazionale di oligoene idrogenate è studiato mediante calcoli quantomeccanici. In particolare, viene analizzato l'andamento delle interazioni tra le coordinate di stretching dei legami CC rispetto alla distanza tra i legami considerati. I calcoli mettono in luce che il valore di tali costanti decresce lentamente con la distanza. Infine, le conseguenze di questo andamento vengono analizzate in relazione alle curve di dispersione fononiche della catena infinita.

Carbon linear chains are interesting π -conjugated systems where long range interactions take place due to the delocalized nature of π electrons. In this contribution the vibrational force field of hydrogen terminated oligoynes of increasing chain lengths is investigated by means of first-principles calculations. In particular it is shown that the interaction force constants between CC stretching coordinates decreases slowly with the distance between the bonds considered. The consequence of such a slow decrease with respect to the phonon dispersion of an infinite chain is discussed.

Keywords linear carbon chains; first-principles calculations; Raman spectroscopy

Introduction

Many experiments [1-4] and theoretical studies [5-13] indicate that linear carbon chains are interesting nanostructured systems for their non-linear optical properties and electronic transport properties. Furthermore, their presence has been recently revealed in carbon clusters and carbon nanotubes [14]. Raman spectroscopy is routinely used for studying carbon nanostructured materials. Therefore, a better knowledge of vibrational properties is highly desirable for a better understanding and characterization of this class of materials.

In this contribution we investigate the vibrational force field of linear carbon chains of increasing lengths and we assess the influence of commonly used functionals in Density Functional Theory (DFT) on the simulation of Raman spectra.

In particular, the decrease of the frequency of the main Raman line upon increasing the length of the carbon chain will be shown to depend critically on the choice of the functional. Minor effects due to the choice of the basis set are also observed.

Analysis of the force field in internal coordinates

Raman spectroscopy is a powerful experimental technique which directly probes the normal modes of vibrations of molecules and solids [15]. In order to most effectively use Raman spectroscopy to get insights into the structure of materials, simulations and theoretical models are often needed, especially when little is known about the system considered. The frequencies of the observed Raman bands are related to the following eigenvalue problem [16]:

$$\mathbf{M}^{-1} \mathbf{F}_x \mathbf{L}_k = \omega_k^2 \mathbf{L}_k \quad (1)$$

where \mathbf{F}_x is the force constant matrix, merely given by the square matrix of the second derivatives of the energy of the system with respect to the vector of the cartesian nuclear displacements \mathbf{x} ; \mathbf{M}^{-1} is the inverse of the diagonal matrix of the nuclear masses; ω_k is related to the vibrational frequency of the k -th normal mode and the eigenvector \mathbf{L}_k represents the direction in space along which the nuclei move in phase during the normal mode of vibration.

While first-principles calculations usually deal conveniently with \mathbf{F}_x in simulating the vibrational spectra, for analysing the results of such calculations an alternative approach employing internal coordinates is advisable. The details of the procedure for constructing internal coordinates and relating cartesian force constants to force constants expressed in internal coordinates can be found elsewhere [16]. We merely recall here that the force constant f_{ij} has to be interpreted as the second derivative of the energy with respect to the internal coordinates R_i and R_j which in our case are simply bond lengths (CC and CH bond lengths). The force constants f_{ij} form a matrix \mathbf{f} which can be represented by using a grey map (see Fig.1 where the matrix \mathbf{f} relative to H-C₁₈-H has been represented). It has to be noticed that no physical information is lost while changing the reference from the cartesian set of coordinates to the internal set of coordinates. This procedure is merely a question of practical convenience either in modelling a proper force field (which is best done in internal coordinates) or analysing the results of first-principles calculations, as in this case.

The plots of Fig.1 give an overall view of the force constant matrix \mathbf{f} for a quite long polyynes, H-C₁₈-H, which extends for about 2 nm from hydrogen to hydrogen. The diagonal of \mathbf{f} (\mathbf{f}_0 vector) collects the spring force constants relative to the bond stretching coordinates along the chain. The co-diagonals $\mathbf{f}_1, \mathbf{f}_2, \dots, \mathbf{f}_s$ collect the interactions between stretching coordinates along the chain which are first nearest neighbours, second nearest neighbours, and so on. The matrix \mathbf{f} is clearly symmetric. The logarithmic left plot of Fig.1 reveals that these off-diagonal interactions die off with respect to the interaction distance s in a less than exponential fashion. Moreover, as the right panel of Fig.1 reveals, a regular and striking alternation of signs is found in the elements of \mathbf{f} . If we restrict the analysis to the sub matrix of the CC interactions, $f(2:18,2:18)$, we can state that the vectors \mathbf{f}_{2s+1} (for $0 \leq s \leq 6$) are

positive, while the vectors \mathbf{f}_{2s} (for $1 \leq s \leq 6$) are negative (the diagonal vector \mathbf{f}_0 is necessarily positive because the system is in a stable minimum). This kind of behaviour has been found in the past for other π -conjugated systems and it has been rationalized based on a physical model relating the interactions between stretching coordinates to the coupling between π -electrons and nuclear motions [17].

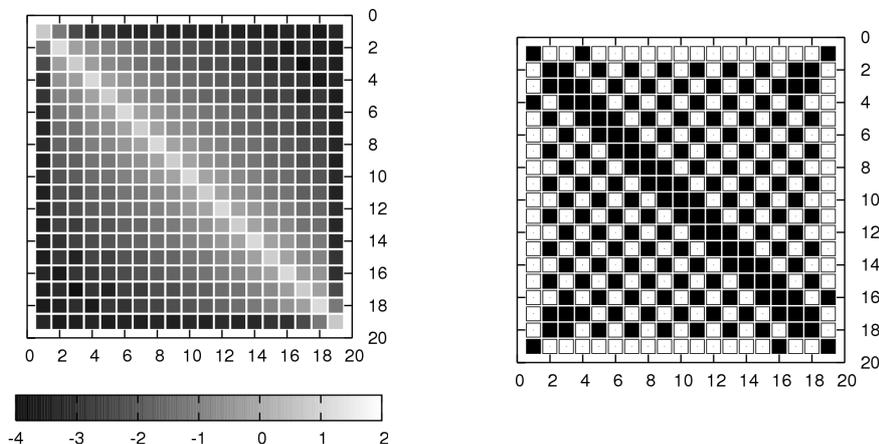


Fig.1 Left: logarithmic grey map of the force constant matrix of the polyene H-C₁₈-H restricted to the bond stretching internal coordinates (the grey map is relative to $\log_{10}|f_{ij}|/f_0$, where f_0 equals to the adopted unit, namely 1 mdyne/Å). The CC stretching coordinates run from index 2 to index 18 and are arranged in an ordered sequence extending from one end of the linear chain to the other. The coordinates number 1 and 20 are CH stretchings. Right: map of the signs of the matrix elements f_{ij} . Positive matrix elements are associated to a filled box; negative matrix elements are associated to an empty box. The data reported here have been obtained with a DFT calculation at the PBE/PBE/cc-pVTZ level.

To better analyse the law of decrease of the off diagonal interactions \mathbf{f}_s with respect to s , a double logarithmic plot is reported in Fig.2 where the average value of $\langle \mathbf{f}_s \rangle$ is plotted against the interaction distance s . Several chain lengths have been considered, ranging from 8 up to 18 carbon atoms. The overall decay of the off diagonal force constants is found to roughly parallel the power law s^{-3} . Decays of force constants interactions less than exponential are expected in other π -conjugated systems affected by Kohn anomaly, such as graphite and nanotubes [18,19]. Recently we have shown that also the infinite linear carbon chain is affected by a Kohn anomaly which explains the behaviour of the force constants reported in Fig.2 [20].

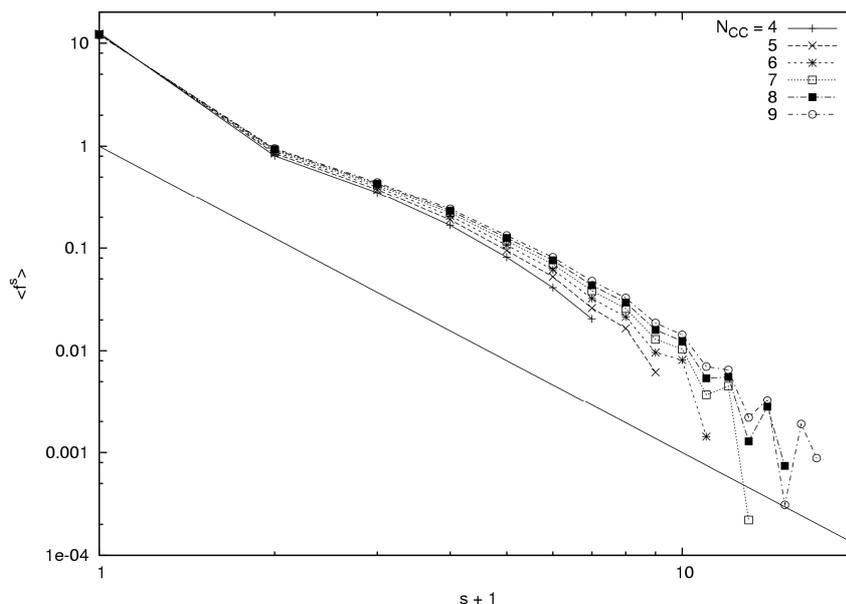


Fig.2 Double logarithmic plot of the decay of the average force constant $\langle f_s^s \rangle$ with respect to the distance of interaction s (see text for the exact definition). The data reported here have been obtained with DFT calculations at the PBE1PBE/cc-pVTZ level carried out for polyynes of increasing lengths, $H-C_{2N}-H$. The continuous straight line is the plot of the function $g(s) = s^{-3}$, reported as a reference.

Based on the results previously shown, it is interesting now to consider how the choice of the functional affects the simulated Raman spectrum. We focus on the longer polyynes, $H-C_{18}-H$, for which the interaction range which can be studied is larger. In Fig.3 we report the average value of the off-diagonal interactions $\langle f_s \rangle$ as a function of the interaction distance s , similarly to the plot of Fig.2. Three different functionals have been considered, the hybrid B3LYP and PBE1PBE and the pure DFT functional BPW91. As the data reported in Fig.3 clearly shows, the inclusion of exact exchange affects the decay slope of the off-diagonal interactions which appears to be steeper. In other words, a pure DFT method predicts longer range vibrational interactions with respect to hybrid DFT. This fact of course affects the simulated Raman spectra which are reported in Fig.4. A longer range of interactions is associated with a significantly lower frequency of the main Raman peak, which down shifts by roughly 200 cm^{-1} while passing from hybrid to pure DFT functional. The effect of the basis set is more limited, as it can be inferred by comparing the BPW91 calculations carried out with Dunning's correlation consistent basis set of double zeta quality (cc-pVDZ) as opposed to a triple zeta quality basis set (cc-pVTZ).

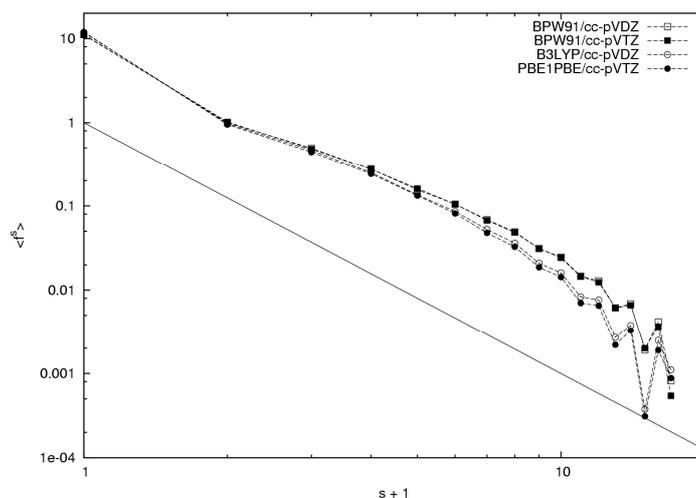


Fig.3 Double logarithmic plot of the decay of the average force constant $\langle f^s \rangle$ with respect to the distance of interaction s (see text for the exact definition). The data reported here have been obtained with DFT calculations at different levels carried out for a long polyyne of fixed length, $H-C_{18}-H$. The continuous straight line is the plot of the function $f(s) = s^{-3}$, reported as a reference.

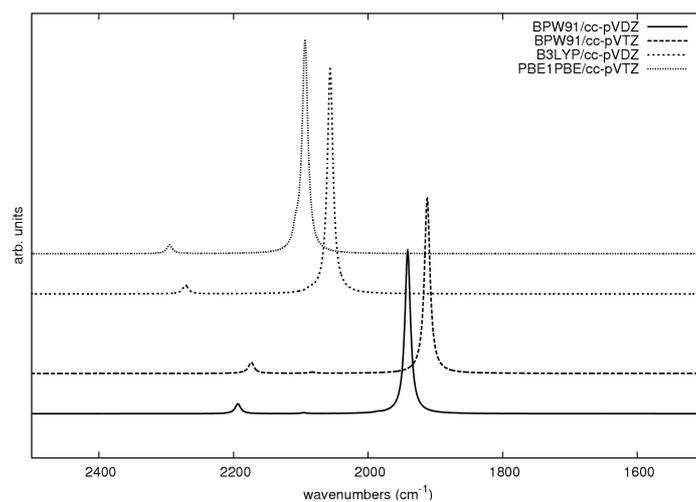


Fig.4 DFT simulations of the Raman spectrum of the longest polyyne here considered, $H-C_{18}-H$. The spectra obtained with the same levels of theory adopted in Fig.3 are here compared. It is evident that the inclusion of exact exchange (PBE1PBE, B3LYP functionals as opposed to BPW91) significantly increases the frequency of the most prominent Raman band by approximately 200 cm^{-1} . On the other hand, the improvement of the basis set (BPW91/cc-pVTZ as opposed to BPW91/cc-pVDZ) brings minor changes in the frequency of this band.

Long range interactions and the infinite linear chain limit

To rationalize why a longer range of interaction is associated to a lower frequency main peak in the Raman a further discussion is needed which takes into account our recent results on the calculations of the phonons of the infinite linear carbon chain [20]. It is possible to show that for the infinite linear carbon chain the phonon associated to the vibration responsible for the main Raman band of finite length polyynes has a frequency given by (at $\mathbf{q} = \mathbf{0}$):

$$\omega^2 = \frac{4F_{\mathcal{R}}}{m}, \quad F_{\mathcal{R}} = \frac{k_1 + k_2}{2} + \sum_{n \geq 1} [f_1^n + f_2^n - 2f_{12}^n] \quad (2)$$

where k_1 and k_2 are the diagonal stretching force constants relative to the two bonds r_1 and r_2 and the terms f^n describe interaction stretching force constants at increasing distances (n) along the chain. Note that the symbol n here has a different meaning with respect to the symbol s employed before, as it is more clearly illustrated in Table 1. The symbol f_i^n refers to the interactions between equivalent bonds belonging to different cells; f_{12}^n refers to the interaction between non-equivalent bonds at distance n . The symbols appearing in Eq. (2) can be collected in a usual matrix representation of the force constant matrix of the infinite chain as follows:

k_1	f_{12}^1	f_1^1	f_{12}^2	f_1^2	f_{12}^3	f_1^3	...
	k_2	f_{12}^1	f_2^1	f_{12}^2	f_2^2	f_{12}^3	f_2^3
		k_1	f_{12}^1	f_1^1	f_{12}^2	f_1^2	f_{12}^3
			k_2	f_{12}^1	f_2^1	f_{12}^2	f_2^2
				k_1	f_{12}^1	f_1^1	f_{12}^2
					k_2	f_{12}^1	f_2^1
						k_1	f_{12}^1
							k_2

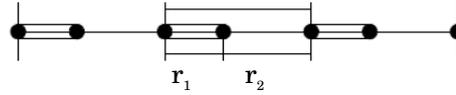


Table 1. Left: symbolic representation of a limited part of the force constant matrix \mathbf{f} of an infinite periodic linear carbon chain (for clarity just the upper triangular part of the symmetric matrix is shown). Shaded matrix elements are positive, accordingly to the findings of Fig.1 and in agreement to previous studies [17]. Right: sketch of the unit cell of the infinite chain with alternated bonds (Peierls distorted [20]).

According to our experience [17] and supported by our present results on oligynes (see Fig.1 and Table 1), we know that the non diagonal CC stretching interactions along CC bonds sequences sharing conjugated π electrons obey to the following general rules:

- (i) the interaction force constants between equivalent bonds (f_i^n) are negative, independently from the kind of bonds;

- (ii) interactions between non-equivalent bonds (f_{12}^n) are positive;
- (iii) the absolute values of the constants f^n slowly decrease with increasing n : due to conjugation, non-vanishing long range interactions take place.

As a consequence of the above rules the sum which appears in Eq. (2) has a negative value, therefore providing a contribution which lowers the force constant F_R and therefore lowers the vibrational frequency ω .

By consequence, according to Eq. (2), there are two mechanisms which determine a softening of the frequency:

- (a) increasing the absolute values of the parameters f^n ;
- (b) increasing the extent of effective interaction (number of terms in the sum).

Based on the conclusions here reached (in particular points (a) and (b) above) we can finally rationalize the results obtained from DFT calculations carried out with different functionals and basis sets. As Fig.3 clearly illustrates, the inclusion of exact exchange in hybrid functionals (B3LYP and PBE1PBE) induces a faster decay of the off-diagonal force constants which is expected to lower the absolute value of the negative sum appearing in Eq. (2). Therefore according to point (a) above the inclusion of exact exchange is expected to increase the frequency of the prominent Raman mode, exactly as Fig.4 demonstrates. As for the basis set effect, which can be better estimated while comparing calculations carried out within the same functional (BPW91), a softer frequency is found for the more extended basis set. This is can be intuitively rationalized by considering that the more extended basis set is expected to describe a more polarizable atom, therefore possibly providing longer range vibrational interactions. The observed decrease of the vibrational frequency of the prominent Raman mode while increasing the length of the linear chain [20, 21] is finally rationalized by means of point (b) above (see Fig. 5).

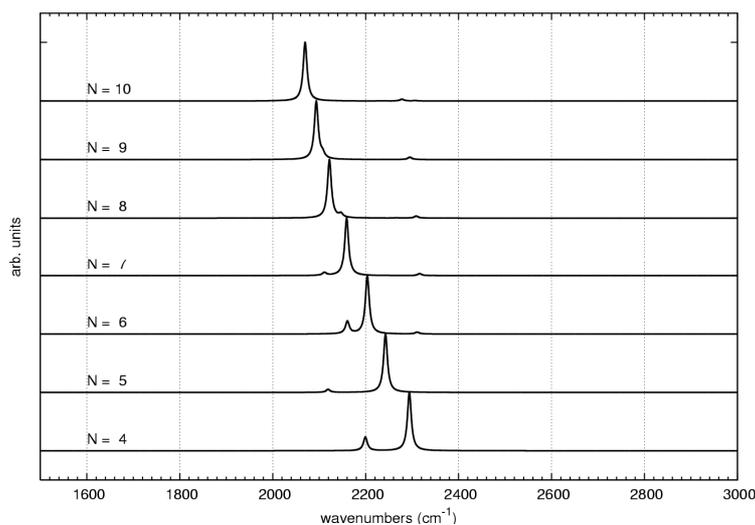


Fig.5 Raman spectra for linear chains of increasing number N of units calculated with PBE1PBE/cc-pVTZ.

Conclusions and perspectives

The role of long range vibrational interactions in linear carbon chains has been discussed aiming at the simulation of Raman spectra. The dependence of the frequency of the prominent Raman mode on the effective range of interaction has been illustrated and rationalized in terms of the results previously obtained for an infinite chain [20]. The relevant increase of the vibrational frequency in long chains due to the inclusion of exact exchange has been discussed. The results here presented should be considered in order to accurately simulate the Raman spectra of sample of polyynes which very recently have become available thanks to chemical synthesis [4].

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