Phonon dispersion and vibronic coupling in carbon nanoribbons

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Abstract. The phonon dispersion curves are presented for a carbon nanoribbon, polyacene. Restricted and unrestricted density functional calculations for \( n \)-oligoacenes \((n = 10 \text{ and } 15)\) predict different spin distributions in the singlet electronic state. The unrestricted states involve spin-localized, singly-occupied orbitals. Bond alternations, infrared activities and phonon dispersions are studied on the basis of these closed-shell and open-shell states, respectively. Vibronic coupling in \( S_0 \leftarrow S_1 \) transitions are investigated using an efficient quantum chemical model (MO/8 model). Franck-Condon and vibronic coupling transitions in oligoacenes are found to be activated commonly, and the vibronic activities are assigned to the same phonon dispersion branches of polyacene.

1. Introduction

Graphene [1], the simplest lattice with the six-fold symmetry, has attracted many researchers in the fields of surface sciences and nanotechnology. On the other hand, molecular systems called polycyclic aromatic hydrocarbons (PAHs) have long been studied both experimentally and theoretically as basic systems possessing \( \pi \) electrons. Nanocarbons, a class of carbon networks with nanoscale sizes lying between these two cases, can be understood within the above frameworks of solid-state physics or \( \pi \)-electron chemistry. Namely, the periodicity in nanocarbons would ultimately converge to the six-fold lattices, whereas the effects of finite sizes and edge structures are connected with molecular properties. However, nanoscale effects arising from the periodic, finite lattices have not been understood well.

One of the ideal cases of the nanocarbons is carbon nanoribbon. They are infinite-length, fine-width honeycomb lattices with the sp\(^2\) hybridisation. The electronic band structures in the ribbons with zigzag or armchair edges have been studied to obtain one-dimensional dispersions [2]. However, the importance of electron-phonon coupling in electron transport strongly demands comparative studies on phonon dispersions. The phonon dispersions and corresponding vibronic coupling have not been fully clarified. Another important issue would be magnetic properties. The infinite carbon lattices are magnetic, in contrast to PAH molecules. Indeed, spin localization has been reported for not only graphene edges [3] but also large linear \( n \)-oligoacenes with \( n > 8 \) [4], where \( n \) is the number of rings.

In this paper, we report on the phonon dispersions of simplest carbon nanoribbons with zigzag edges, polyacenes, in different electronic configurations. Those dispersion curves are constructed extrapolatively from the force fields of \( n \)-oligoacenes with \( n > 8 \). Spin localization is also studied.

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employing unrestricted quantum chemical calculations. They are compared with the previous results of restricted calculations [5,6].

2. Calculations
Density functional calculations were performed with a Gaussian 03 program on Linux-based computers and/or a supercomputer (Fujitsu Primequest) at the Research Center for Computational Science of the National Institutes of Natural Sciences. Becke’s three-parameter gradient corrected exchange and the Lee-Yang-Parr gradient-corrected correlation functionals (B3LYP) were employed throughout this work on the basis of the 4-31G functions. Harmonic frequencies were calculated at optimized geometries without scaling to avoid inconsistency between frequency and intensity.

The force constants for polyacene were constructed from zone folding approach for pentadecacene ($n = 15$). The analytic force constants were folded into the force constant matrix ($F$ matrix) for the unit cell in the Brillouin zone by weighting the phase factor, $\theta$, in the Cartesian-coordinate space:

$$F = \sum F^{(k)} \cos k \theta$$

where $F^{(0)}$ is the internal $F$ matrix of the repeating unit, and $F^{(k \neq 0)}$ are those for off-diagonal $F$ matrices for interaction with the $k$th neighbouring unit. Vibronic bands were calculated using an efficient quantum chemical model (MO/8 model) [7,8]. Briefly, force fields were obtained by scaling bond orders and bond-bond polarisabilities with 8 fixed, transferable parameters. The transitions to the electronic excited states were calculated under the Pariser-Parr-Pople approximation for self-consistent field (SCF) configuration interaction (CI) calculations, combined with Nishimoto-Mataga approximation.

3. Results and Discussion
Unrestricted occupied spatial orbitals in the singlet state correspond to open-shell diradical states, in which the singly-occupied orbitals exist along the CCC ribbon on each side [4]. The open-shell configuration is predicted to give the ground state for decacene. These diradical states are important in the ‘transition’ regimes between PAH molecules and magnetic carbon networks. In this context, polyacene is a basic model system, although quantum chemical calculations for polyacene have only been directed to its aromaticity and bond alternations in the restricted states [9-13]. Bond alternation and spin localization are likely to relate to the nanoscale effects in nanocarbons [3].

The open-shell diradical state is calculated to be 20.0 kcal mol$^{-1}$ lower than the restricted closed-shell state. Table 1 presents the degrees of bond alternations for pentadecacene ($n = 15$). The first row corresponds to the bonds in the central unit cell, and these values are expected to be more independent of the edge structures than at terminal. In both open-shell and closed-shell states, shrinking (expanding) behaviours are clearly obtained for outward (inward) CC bonds, respectively, towards the maximum alternation at terminals.

| Inward CC | Outward CC | Joint CC |
|-----------|------------|----------|
| Open      | Closed     | Open     | Closed   | Open     | Closed   |
| 1.405     | 1.404      | 1.405    | 1.403    | 1.461    | 1.469    |
| 1.405     | 1.405      | 1.406    | 1.403    | 1.462    | 1.469    |
| 1.403     | 1.406      | 1.407    | 1.402    | 1.463    | 1.469    |
| 1.400     | 1.408      | 1.410    | 1.401    | 1.463    | 1.468    |
| 1.399     | 1.411      | 1.412    | 1.398    | 1.461    | 1.466    |
| 1.407     | 1.419      | 1.410    | 1.394    | 1.456    | 1.463    |
| 1.430     | 1.437      | 1.397    | 1.385    | 1.450    | 1.460    |
|           |            | 1.370*   | 1.364*   | 1.426    | 1.434    |

*Terminal parameters are printed in italics.
The almost identical bond distances in central parts (given in upper rows) would ultimately converge to the periodicity of infinite lattices. The experimental bond distances of hexagonal systems of graphite and benzene are 1.42 Å and 1.397 Å, respectively. Therefore, these inward and outward CC bond distances are close to that of benzene, whereas the joint CC bonds are much longer. These tendencies are due to particular structural deviations in acenes from the regular hexagonal lattices. The C_{2h} symmetry type of bond alternations in a trans form was not obtained in this work.

Figure 1 compares calculated infrared spectra between open-shell and closed-shell singlet states of decacene (n = 10). Again, the open-shell state is calculated to be 8.6 kcal mol⁻¹ lower than the closed-shell state, which is in line with the previous results at BPW91/6-31G(d) and BLYP/6-31G(d) levels of theory [4]. The infrared spectra of the two states display similar bands in frequency and intensity, except for the in-plane joint CC stretching bands (CC ip edge and \(v_2\)) obtained at ~1550 cm⁻¹ in the open-shell state. The infrared intensity obtained in the short axis direction strongly suggests contribution from the singly-occupied orbitals delocalized over the CCC perimeter at each side.

Figure 2 compares vibrational dispersion relations for all modes of polyacene in the open-shell and closed-shell states. The vibrational modes of finite systems are well explained in terms of the phase difference of the infinite system, \(\theta\). For example, the band progressions calculated at ~950 cm⁻¹ in Figure 1 correspond to CH out-of-plane modes with different phases of displacements. They show different phases in vibrational displacements between neighbouring CH bonds. The calculated dispersion curves are found to be very similar between the open-shell and closed-shell states, except in-plane branches \(v_3\) and \(v_4\). Hence, the frequencies of these modes can act as marker bands of localized spin states, in addition to the above mentioned infrared activities. These modes are characterised to be perimeter CC displacements in the same direction.

Next, we show electron-phonon (vibronic) coupling on the basis of molecular spectroscopy. Figure 3 depicts the calculated transition intensities for vibronic bands associated with \(S_1\rightarrow S_0\) transitions of octacene (n = 8) and decacene. Interestingly, the vibrational modes of both acenes display similar intensity patterns. Moreover, the major infrared activities are similarly obtained for acenes with n = 4, 5 [Ref. 5], 8 and 10, and their vibrational patterns are categorised in the same branches of
dispersion curves in Figure 2. The Franck-Condon type transitions are obtained for \( a_g \) modes \((\nu_1, \nu_4 \text{ and } \nu_6)\) upon this electronic transition of the \( 1L_a \) type, whereas the vibronic-coupling transitions are activated for \( b_{3g} \) modes through interaction with higher electronic states of the \( 1B_b \) type. Since the activities given in Figure 3 are those for vibrational states of the electronic ground state, these distributions correspond to resonance Raman effects. It should be noted that the scales between the two types of transitions are arbitrary. Decacene tends to display stronger intensities of the VC type relative to those of FC type than octacene.

Vibrational frequency shifts towards low wavenumber on going towards larger acenes are explained by the decreased phase difference between neighbouring units. The phase difference becomes smaller since the vibrational displacements must minimize \( \theta \) to gain optical activities under the boundary conditions within the lengths of molecules. In particular, the remarkable shifts for mode \( \nu_6 \) are due to the acoustic modes that converge to translational or rotational motion at \( \theta = 0 \). The phase difference seems to affect the transition intensities of these molecules, since only a few vibrations display vibronic activities among many vibrations with different phases. The vibrations of these non-hexagonal distorted carbon networks in the region 1000-1350 cm\(^{-1}\) with particular phase relations are expected to show strong resonance Raman effects of FC types.

4. Conclusions
The phonon dispersions of open-shell and closed-shell singlet states are similar except the perimeter symmetric CC modes. The vibrational bands of large acenes display low-wavenumber shifts systematically on going towards longer systems, whereas the vibronic activities appear very similarly. This work illustrates the possibility of molecular spectroscopic approaches to problems of nanocarbons.

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