Resonance Raman study of polyynes encapsulated in single-wall carbon nanotubes

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This work presents a resonance Raman study of polyyne molecules (linear carbon chains) encapsulated inside single-wall carbon nanotubes using many different laser lines. A strong enhancement of the polyyne Raman features is observed around 2.1 eV, and this result is ascribed to dark electronic transitions of the linear carbon chains that can be observed when they are trapped inside a carbon nanotube. The huge observed energy splitting between bright and dark excited states is ascribed to strong Coulomb effects in this strictly one-dimensional system.

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Polyyne molecules are linear carbon chains, with alternating single and triple bonds, and terminated by end atoms or groups. This kind of structure is of fundamental interest since it is the perfect example of a purely *sp*-hybridized carbon structure, which is expected to show a completely different physics than the more common sp^2 and sp^3 carbon structures. Moreover, they represent the ultimate linear wire, which may not only transport charge between its ends through their π electrons but also serve as a perfect playground for studying the strong and unique effects of electron correlations in one-dimensional systems. However, the study of the physical and chemical properties of these linear molecules has been hindered by the fact that they are very unstable at normal temperature and atmosphere conditions.[1,2] Very recently, polyynes have been encapsulated inside single-wall carbon nanotubes (SWCNTs).[3] Trapped inside SWCNTs, these molecules can be carefully studied experimentally, allowing a complete understanding of their electronic structure, a crucial step toward future applications of these systems. In this work, we present a resonance Raman study of encapsulated polyynes, and the results reveal important many-body physical effects in this best prototype of a one-dimensional system.

Hydrogen-ended polyyne molecules, $H(—C{\equiv}C—)_nH$ or just $C_{2n}H_2$, are the simplest polyyne molecules and have been produced recently by techniques of graphite ablation in organic solvents.[4,5] Nishide *et al.*[3] were able to encapsulate $C_{2n}H_2$ polyynes ($n=5$) inside single-wall carbon nanotubes (SWCNTs) and have shown that these molecules can be stable even at high temperatures, up to 350 °C. Linear chains of carbon atoms have also been observed inside multiwall carbon nanotubes[6] and on double-wall carbon nanotubes heat treated at high temperatures.[7,8] All these *sp*-hybridized systems exhibit Raman features in the range 1800–2100 cm^{-1}, depending on the chain size and environment[3,8,9] and if their ends are free or fixed to the nanotubes.

This work presents a resonance Raman study of two polyyne molecules ($C_{10}H_2$ and $C_{12}H_2$) encapsulated inside single-wall carbon nanotubes (SWCNT). By using many different laser lines covering the whole visible range, we show that the main Raman features associated with stretching modes of the linear chains in both samples ($C_{10}H_2$@SWCNT and $C_{12}H_2$@SWCNT) are strongly enhanced around 2.1 eV, whereas the optical absorption observed when these molecules are dispersed in isotropic medium[9] or in the gas phase[10] occurs at much higher energy (above 4.5 eV.). The results are interpreted here in terms of dipole-forbidden (dark) transitions of the polyynes that become active due to a symmetry breaking when the molecules are encapsulated and discussed in terms of many-body physics in an atomic linear chain.

The $C_{10}H_2$ and $C_{12}H_2$ polyynes were made by laser ablation of graphite particles in *n*-hexane, and the molecules with different sizes were separated by high-performance liquid chromatography.[4] The SWCNTs were prepared by laser ablation of metal-containing carbon rod. The diameter distribution of the obtained SWCNTs, estimated from the radial breathing mode of the Raman spectra, is 1.3 ± 0.2 nm.[3] For encapsulating the polyynes inside the SWCNTs, a piece of nanotube film was dipped inside the separated polyyne dispersion in *n*-hexane and kept at 80 °C for 24 h under vacuum.[3] The samples were carefully washed by *n*-hexane after the encapsulation treatment, and the polyynes attached outside were completely washed out by solvents.[3] Raman scattering experiments were performed at room temperature using a triple monochromator micro-Raman spectrometer (DILOR XY). The laser power used was 1 mW with a spot diameter of ~1 μm using a 80× objective. We used five different laser lines of an Ar-Kr laser (1.92, 2.18, 2.41, 2.54,

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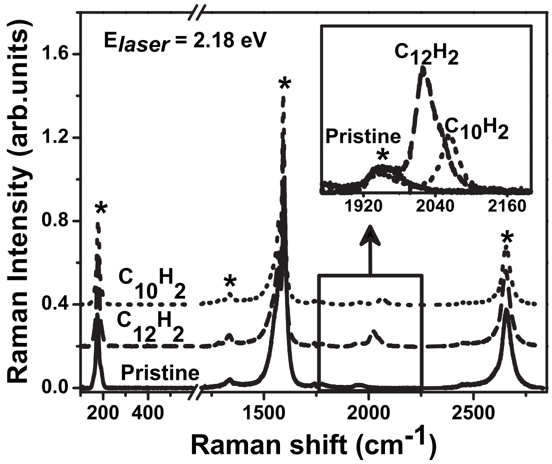

FIG. 1. Raman spectra with 2.18 eV excitation energy for the different samples: $C_{10}H_2$@SWCNT (dotted and top spectra), $C_{12}H_2$@SWCNT (dashed and middle spectra), and pristine SWCNT (solid and bottom spectra). The inset shows a larger view of the *P* bands for the two polyyne samples. The asterisks indicate the most prominent Raman features of SWCNTs

and 2.71 eV) and 15 laser lines from a dye laser ranging from 1.9 to 2.3 eV.

Figure 1 shows the Raman spectra, recorded using the 2.18 eV (568 nm) laser line, of the carbon nanotube pristine sample (spectrum at the bottom of the figure) and of the two samples of $C_{10}H_2$ and $C_{12}H_2$ polyynes encapsulated in SWCNTs. All peaks in this figure marked by asterisks are associated with the most prominent Raman features of the carbon nanotubes,[11] such as the radial breathing mode (RBM) around 200 cm^{-1} and the *D*, *G*, and *G'* peaks around 1350, 1590, and 2700 cm^{-1}, respectively. The bands in the range 2000–2100 cm^{-1}, denoted here by *P* bands, are associated with the stretching vibrations of the polyynes inside the nanotubes.[12]

In the case of the $C_{10}H_2$@SWCNT sample, the *P* band is composed by just one peak, centered at 2066 cm^{-1}, and it is associated with the ν_3 vibrational mode of the polyyne chain.[12] The *P* band of the $C_{12}H_2$@SWCNT sample is clearly composed by two peaks, centered at 2020 and 2050 cm^{-1}, and they have been ascribed to the ν_4 and ν_3 vibrational modes of the $C_{12}H_2$ molecule inside the carbon nanotube.[12] As a general trend, the frequency of the main Raman feature of the $C_{2n}H_2$ polyynes is inversely proportional to the number $2n$ of carbon atoms in chain.[9] These frequencies also depend on the environment of the polyyne. Nishide *et al.*[3] have shown that the frequencies of the *P* bands for the $C_{10}H_2$@SWCNT and $C_{12}H_2$@SWCNT samples are downshifted with respect to those of the $C_{10}H_2$ and $C_{12}H_2$ polyynes dispersed in *n*-hexane [57 cm^{-1} for $C_{10}H_2$ and 33 cm^{-1} (ν_4) and 47 cm^{-1} (ν_3) for $C_{12}H_2$].

In this work, we will focus on the resonance behavior of the *P* band by inspecting the laser energy dependence of this band. We recorded 18 spectra similar to those of Fig. 1 by changing the laser energy between 1.90 and 2.71 eV, and, in the following, we will discuss the modifications that are observed in the *P* band when we change the laser energy. We have also measured the optical absorption spectra in the visible range of the $C_{10}H_2$@SWCNT and $C_{12}H_2$@SWCNT samples dispersed in water, and we have observed many peaks which are associated with the many different (n,m) nanotubes present in the sample, superimposed with the peak of the polyynes. However, we could not distinguish in the optical absorption spectra the contribution of the nanotubes from that of the polyynes, contrary to the case of a resonant Raman experiment, in which we can clearly distinguish the contribution of each specific (n,m) nanotube[13] and that of the polyyne.

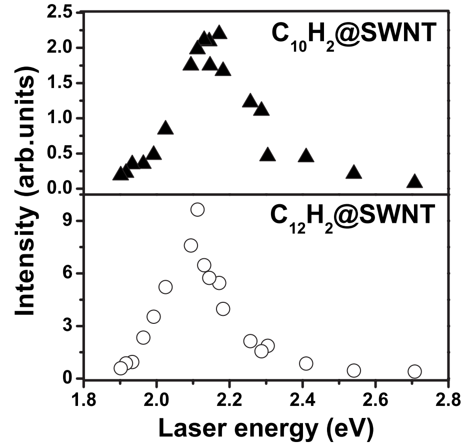

FIG. 2. Raman intensity of the *P* bands for $C_{10}H_2$ (closed triangles) and for the $C_{12}H_2$ (open circles) as a function of laser excitation energy.

The inset of Fig. 1 shows the detailed spectra of the *P* band for $C_{10}H_2$@SWCNT and $C_{12}H_2$@SWCNT as well as the spectrum of the pristine SWCNT sample in this frequency range. Notice that the spectrum of the pristine sample also exhibits a weak band around 1950 cm^{-1}, which is a common feature to all kind of graphitic (sp^2) materials and that is ascribed to a second-order Raman process involving the combination of two phonons within the interior of the first Brillouin zone of graphite.[14] Since these second-order features are known to exhibit a strong dispersion when the laser energy is changed, we have measured the laser energy dependence of the frequency of the Raman peaks of $C_{10}H_2$@SWCNT in the range 1900–2100 cm^{-1}. We have observed that the frequency of the second-order feature strongly depends on the laser energy, whereas the frequency of the *P* band remains constant by changing the laser energy. A similar behavior was observed for the $C_{12}H_2$@SWCNT sample. The nondispersive behavior of the *P* band confirms that it is a first-order Raman feature and necessarily associated with the *sp*-carbon linear chain.

In order to analyze the laser energy dependence of the *P* band intensity, all spectra were normalized to keep the intensity of the *G* band of the carbon nanotube constant. Due to the large number of nanotube species in the sample, the *G*-band intensity is not expected to depend significantly on E_{laser} and, thus, it can be considered as a good internal parameter for normalization. Figure 2 shows the laser energy dependence of the intensity of the *P* band for the $C_{10}H_2$@SWCNT and $C_{12}H_2$@SWCNT samples. There is a

TABLE I. Bond-length alternation (BLA) in the center of the chain (in Å) and optical transition energies (in eV) for $C_{10}H_2$ and $C_{12}H_2$. "Geometry" indicates the geometry optimization method.

			TDDFT			ZINDO		
Molecule	Geometry	BLA	Σ_u^-	Δ_u	Σ_u^+	Σ_u^-	Δ_u	Σ_u^+
$C_{10}H_2$	PBE1PBE	0.116	2.76	2.89	5.20	2.20	2.50	5.50
	BHandHLYP	0.143	3.10	3.25	5.74	2.46	2.76	5.68
$C_{12}H_2$	PBE1PBE	0.109	2.48	2.59	4.65	2.03	2.31	5.07
	BHandHLYP	0.140	2.87	3.00	5.24	2.31	2.60	5.26

clear resonance enhancement in the intensity of these bands between 2.0 and 2.3 eV, the maximum occurring at approximately 2.14 and 2.10 eV for the $C_{10}H_2$@SWCNT and $C_{12}H_2$@SWCNT samples, respectively.

It is important to emphasize that the RBM bands of the different (n,m) SWCNTs have been observed in all spectra recorded with the different laser lines shown in Fig. 2. Since the observation of the RBM spectra is due to a resonance phenomena in SWCNTs, the fact that the enhancement of the polyyne Raman peak occurs only around 2.1 eV clearly shows that this resonance cannot be associated with the electronic transitions of the nanotubes, but, in fact, with the intrinsic transitions of the polyynes.

The electronic transitions of different $C_{2n}H_2$ polyynes in gas phase[10] and in neon matrixes[15] have been measured by absorption spectroscopy. The strong UV absorption observed for the $C_{2n}H_2$ molecules with a small number of carbon atoms was interpreted based on quantum chemistry models as arising from the transition between the ground state and the first dipole-allowed transition of the molecule. The energy of this electronic transition was observed to increase with decreasing value of n.[15] From Ref. 10, one can estimate the gas phase values for the UV transition energy to be 5.4 eV for $C_{10}H_2$ and 5.0 eV for $C_{12}H_2$.

Tabata *et al.*[9] reported recently the UV absorption spectra of different $C_{2n}H_2$ polyynes dispersed in n-hexane, and, for each value of n, the spectrum was composed by peaks separated by the energy of one stretching mode of the linear chain (a vibronic spectrum). In the case of the $C_{10}H_2$ and $C_{12}H_2$ molecules, the longest wavelength peak observed in the UV absorption spectra and that corresponds to a zero-phonon process was observed at 4.90 and 4.50 eV for the $C_{10}H_2$ and $C_{12}H_2$ polyynes, respectively. Notice the strong redshift due to solvent effects, as compared to the gas phase transitions.

We explain the resonance behavior observed in this work around 2.1 eV as due to resonances with lower energy electronic transitions in the polyynes that are not allowed when the molecule is surrounded by an isotropic medium. When the polyyne is encapsulated in the interior of a single-wall carbon nanotube, the axial site symmetry is broken due to the interaction with the nanotube wall, and new electric dipole electronic transitions can be activated in this case. In order to check this explanation, we performed time-dependent density functional theory[16] (TDDFT) and semiempirical ZINDO[17] calculations of the optical spectra of $C_{10}H_2$ and $C_{12}H_2$. Since the electronic structure of these molecules critically depends on the degree of carbon-carbon bond-length alternation (BLA) along the chain,[18] we took extra care in determining the molecular geometries. It is well known that pure density functional theory (DFT) functionals do not describe the BLA of such systems in an accurate way. Usually, hybrid DFT methods (mixing with exact exchange) perform better, and the BLA typically increases with the amount of exact exchange.[18] We performed geometry optimization with two hybrid schemes: PBE1PBE,[19] which mixes 25% of exact exchange, and BHandHLYP,[20] which mixes 50%. BHandHLYP describes well the BLA of the related systems polyacetylene and polydiacetylene.[18] We used the GAUSSIAN03 program[20] with the 6-31G* Gaussian-type basis sets.

The nature and symmetries of the excited states in the polyynes can be understood in a simple way. Both the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are doubly degenerate, transforming according to the Π_g and Π_u representations of the $D_{\infty h}$ point group, respectively. They correspond to bonding and antibonding combinations of p_x and p_y orbitals at the triple bonds. If we restrict our reasoning to single excitations within these four orbitals, the excited states should transform as $\Pi_g \otimes \Pi_u = \Sigma_u^- + \Sigma_u^+ + \Delta_u$. From these states, only Σ_u^+ is dipole allowed, with the others being forbidden (dark) states.

Our results are summarized in Table I. As expected, BHandHLYP gives a larger BLA than PBE1PBE, and the optical transition energies are strongly dependent on geometry. Also, even for a given geometry, there is substantial scattering in the theoretical transition energies, indicating the degree of uncertainty at this level of calculation. We find the dipole-allowed states with Σ_u^+ symmetry between 5.2 eV and 5.7 eV for $C_{10}H_2$ and between 4.7 eV and 5.3 eV for $C_{12}H_2$, depending on the BLA. These values compare rather well to the gas phase transition energies.[10] The dark states with Σ_u^- and Δ_u symmetries are found at much lower energies: from 2.2 to 3.3 eV for $C_{10}H_2$ and from 2.0 to 3.0 eV for $C_{12}H_2$. These values are very close to our measured resonances in encapsulated polyynes.[21] Notice the huge ($\sim$2.5 eV) splitting, due to Coulomb interactions, between bright and dark many-electron states which are essentially composed by different linear combinations of the same set of single-particle states. For comparison, similar bright-dark splittings in carbon nanotubes are of the order of tens of meV.[22] Moreover, the $\Sigma_u^- - \Delta_u$ energy splittings are roughly 0.1–0.3 eV for the two molecules, also in good agreement with our resonance width.

We therefore propose that our observed resonances between 2.0 and 2.3 eV are due to the dipole-forbidden Σ_u^- and Δ_u states of the polyynes. These transitions are made "bright" due to a lowering of the site symmetry from $D_{\infty h}$ to C_{2v} when the encapsulated molecules are displaced from the central axis of the nanotube. Indeed, for the diameter range of nanotubes considered in our study, there is plenty of room for the polyynes to adopt an off-center position, close to the inner wall of the tube, due to attractive noncovalent interactions. In order to support this interpretation, we have measured three polyyne@SWCNT samples with different mean nanotube diameters (1.3, 1.4, and 1.5 nm),[12] and we have observed that the intensity of the polyyne Raman peak decreases with decreasing mean nanotube diameter, where the axial symmetry breaking is expected to be weaker, thus confirming the hypothesis that the enhancement of the polyyne Raman peak around 2.1 eV is related to the axial site symmetry breaking.

In summary, we have measured the resonance Raman spectra of two polyyne molecules ($C_{10}H_2$ and $C_{12}H_2$) encapsulated inside SWCNTs with many different laser excitation energies in the range of the visible. We observed that the intensity of the Raman band associated with the stretching mode of the linear chain inside the nanotube is strongly enhanced for laser energies around 2.1 eV. This energy value is much lower than the absorption peaks of the $C_{10}H_2$ and $C_{12}H_2$ polyynes dispersed in organic solvents (4.9 and 4.5 eV, respectively) or in the gas phase (5.4 and 5.0 eV, respectively). The resonance Raman behavior observed here is interpreted in terms of dipole-forbidden transitions of the polyynes that are made bright due to a breaking of $D_{\infty h}$ site symmetry when the molecules are encapsulated. Our combined experiment-theory determination of a huge ($\sim$2.5 eV) energy splitting between bright and dark excited states sets the scale of the strong Coulomb effects in the most extreme one-dimensional system, an atomic linear chain.

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