Electronic structures of one-dimension carbon nano wires and rings

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Abstract. The electronic structures of one-dimension carbon nano wires, nano rings of C_{10} to C_{22} and hydrogen end-capped carbon nano wires of HC_{2n}H (n=8-13) have been investigated based on time-of-flight (TOF) mass spectroscopy, laser spectroscopy and first principle ab initio calculations. The size-selected carbon nano molecular wires and rings were investigated on-line using a two-color laser spectroscopic method. The ab initio predicts that the linear structures of the pure carbon nano molecular wires are about 3 eV higher in energy compared to those of the ring structures with similar size. The ring structure with bond length alternation (Peierls'dimerization) is unstable at size up to C_{22} ring. The optical transition energies were calculated using the time-dependent density functional theory (TD-DFT) and the CASSCF approach. For longer wires, it seems that the C_{4n+2} wires are metallic and the hydrogen end-capped carbon wires could be semiconductors.

1. Introduction
Molecular wires are proposed to be used in molecular electronic and optoelectronic devices to replace metal and silicon-based wires in semiconductor devices.[1] Organic molecular wires such as oligo(2,5-thiophene ethynylene)s, oligo(1,4-phenylene ethynylene)s, oligo(1,4-phenylene vinylene)s, polyphenylenes, acetylene oligomers and organometallic molecular wires have been extensively investigated using various methods.[2] These wires consist of conjugated hydrocarbon molecular chains and aromatic hydrocarbon molecular rings. The fully conjugated organic aromatic molecular wires are believed to be the best candidates for introduction into new electronic devices as replacements for the Al or Cu wiring used in logic and memory devices.[1]

One-dimension (1D) pure carbon molecular wires and rings are also attractive candidates due to their double aromatic structures.[3-4] They are ideal model systems for studying the electronic structure of low dimension systems and also have potential applications in nano-science, molecular device design and astrophysics.[5-7] Nano carbon systems (such as chains, rings, fullerenes, and grains) are also believed to exist in the interstellar medium (ISM).[8] Studies of the electronic structures and the size-dependent quantum effect of these nano-scale carbon building-blocks are an important step toward their practical applications. To this aim, a novel experimental approach, based on a two-color laser spectroscopic technique coupled with a pulsed discharge or laser ablation source, has been developed in our group.[5-7] In this paper we present further theoretical calculations and experimental
spectral data to investigate the electronic structure of the 1D carbon nano molecular wires and rings and the hydrogen end-capped nano molecular wires. These results give insight into the electronic structures of the various systems, in particular, the band’s structures and quantum size effects.

2. Experiments
The experimental set-up consists of a two-color laser spectroscopic system combined with a molecular-beam time-of-flight (TOF) mass spectrometer. Either a discharge source was used to produce hydrogen end-capped carbon nano wires, or a laser ablation source was used to generate pure carbon nano wires and rings. The hot plasma produced from the discharge or laser ablation source was supersonically expanded into vacuum and entered an extraction-zone through a 2-mm skimmer. All ions were removed by an electric field perpendicular to the molecular beam after the skimmer and before entering the TOF. The neutral molecules were then ionized via laser radiation absorption by the two-color one-photon excitation plus one-photon ionization (1+1’) method. The ions were extracted in a two-stage acceleration setup toward a micro-channel plate (MCP) detector. The signal from the MCP detector was fed into an ultra fast oscilloscope after pre-amplification and transferred to a computer. The mass resolution (\(\Delta m/m\)) of the instrument is approx. 900. Gates were set on the mass spectrum and the ion signal was recorded versus the laser wavelength, enabling a simultaneous scan of many different masses. Up to 200 gates have been concurrently measured.

The two-color laser spectrum (1+1’) was recorded in the UV and in the visible range. The excitation photons were delivered by the frequency doubled output of a dye laser pumped by a Nd:YAG laser or by a commercial OPO system. The ionizing photons came from an excimer laser (F2 at 157 nm or ArF at 193 nm).

3. Experimental results
3.1 TOF Mass spectroscopic characterization
A mass spectroscopic method was used to characterize the distribution of the nano carbon molecular wires and rings produced by the discharge and laser ablation sources. The pulse discharge source is very efficient in producing hydrogenated carbon wires and rings. A mass spectrum of a diacetylene/Ar discharge is shown in Fig.1. In the mass spectrum, the group with small masses consists of hydrocarbon species and the group with large masses is dominated by fullerenes (from C_{36}-C_{114}). The zoom indicates the hydrocarbon species with sizes from C_{24} to C_{24}H_{m} (m=1-11).

![Mass spectrum of HC_{2}H/Ar discharge.](image1)
![Mass spectrum of laser ablation graphite.](image2)

Using the discharge source one can also produce pure carbon nano wires and rings, however the efficiency is very low (see Fig.1). This is because the generated pure carbon wires are chemically unstable and easily react with hydrogen to produce hydrocarbon species. In order to produce pure
carbon nano species we have developed a laser ablation source using a graphite rod. This source is very efficient and generates pure carbon species from C_{9} to C_{34} (Fig.2). It is also very stable from shot to shot and allows one to measure optical spectra using laser spectroscopic techniques.

3.2 Optical spectra of carbon wires and rings
Optical spectroscopy is an important tool for investigating the electronic states and band structures of carbon nano molecular wires and rings. A two-color laser spectroscopic method was used to measure the electronic spectra of the hydrogenated carbon wires, as well as pure carbon wires and rings. Only the spectra of the hydrogenated carbon wires of HC_{16}H to HC_{26}H and the pure carbon rings of C_{14}, C_{18} and C_{22} were observed. The spectral analysis has been carried out in previous publications. Previous analysis of the spectral data revealed that the wavelengths of the origin bands of HC_{16}H to HC_{26}H increase near-linearly with the size of the chains. A similar but linear behavior has been found for C_{2n}H^{+} wires with negative charge (Fig.3). This indicates that the optical bands of the carbon wires exhibit a size-dependence effect.

![Figure 3. Optical wavelength vs. the size.](image)

![Figure 4. Optical transition energy vs. the size.](image)

4. Theoretical calculations
In order to understand the reason for the size-dependence effect, a simple ‘particle in box’ model has been used for analysis (see reference [5]). The model of an electron in a 1D box (free electron model) predicts a linear dependence of the optical band wavelength on size. This is the case for C_{2n}H. On the other hand, the experimental data demonstrate a near-linear dependence of the optical band wavelength of HC_{2n}H on the size (Fig.3). This is due to the model of the ‘particle in box’ being too simple. A real carbon molecular wire involves many electrons (in particular, valence electrons). Electron correlation thus plays a very important role in the electronic structures. In this contribution, we have carried out first principle ab initio calculations on the electronic structures of the hydrogenated carbon wires, pure carbon wires and rings using the density functional theory (DFT) and time-dependent density functional theory (TD-DFT). The hybrid functional of the B3LYP has been used for our calculations. The B3LYP functional has the form:

\[
0.2E_{\text{exact}} + 0.72E_{\text{B88}} + 0.08E_{\text{Slater}} + 0.81E_{\text{LYP}} + 0.19E_{\text{VWN5}}
\]

which includes exact Hartree-Fock exchange, Becke 88 exchange, Slater exchange, the gradient LYP correlation and the VWN5 for local correlation. For the smaller C_{14} carbon wire and ring, the coupling cluster (CCSD(T)) approach was applied. The TD-DFT theory was used for predicting the optical
bands for the pure carbon wires and rings. The CASSCF approach \cite{13} was used for calculating the electronic transition energies of the hydrogen end-capped carbon wires of HC_{2n}H. The Pople’s type atomic basis set of 6-31G* (double Zeta +polarization) was used. The calculations were carried out using GAUSSIAN 03 suite of programs \cite{14} and MOLPRO 2K package \cite{15}.

5. Theoretical results

5.1. Structures and stability of carbon wires and rings
The B3LYP calculations predicted that rings with bond angle alternation are the most stable structures. The DFT calculations indicated that the most stable structure for C_{14} is a ring with bond angle alternation, but the CCSD(T) showed that the ring with perfect aromatic structure (D_{14h} symmetry) is the lowest in energy. Linear structures of the pure carbon nano molecular wires were predicted to lie about 3 eV higher in energy compared to the rings of similar size. The B3LYP calculations showed that ring structures with bond length alternation (Peierls’ dimerization \cite{16-17}) are unstable at sizes up to C_{22}.

5.2. Energy gap and optical bands vs. size
For the hydrogen end-capped carbon wires of HC_{2n}H (n=2-12), a few optical transition systems were calculated using the CASSCF approach with an active space of CAS (12,12). The calculated electronic transition energies qualitatively agree with those observed from the spectroscopy (see Fig.4). A large error between the calculation and experiment is due to the fact that not enough electron correlation energy is included in the CASSCF approach.

For pure carbon wires and rings, the DFT calculations predicted that the energy-gap of $\Delta_{\text{HOMO-LUMO}}$ and the transition energies of the band systems decrease with the size of the molecules (Fig.5). The band-gap of the ring is larger than that of the corresponding wire because the ring has a closed-shell electronic structure while the wire possesses an open-shell structure. These are in agreement with the experimental results from the observed spectra \cite{7}.

5.3. The IP, EA and electronic chemical potential vs. size
For both wires and rings, the ionisation potential (IP) decreases with size while the electron affinity (EA) increases (see Fig.6). The rings have much lower EAs than the wires of the same composition. The chemical potential of the rings slightly increases while the chemical potential of the wires slowly decreases with size.

6. Concluding remarks
The calculations reveal that for pure carbon wires the convergence to the bulk behavior is fast and a small optical band-gap of ~0.6 eV persists in the size as long as ~2.8 nm. For pure carbon rings the convergence to bulk behavior is slower than the wires and an optical band-gap of ~1.7 eV remains in the size of ~2.8 nm (Fig.5). For the hydrogen end-capped carbon wires, the convergence to bulk behavior is extremely slow and a significant optical band-gap of ~2.5 eV persists in the size of ~3 nm (Fig.4). Bond length alternation was found for both the pure carbon wires and the hydrogen end-capped carbon wires, but not for the pure C_{4n+2} rings (n=2-5).

The bond length alternation and the electron localization induce an energy-gap near the Fermi level and reduce the electrical conduction. For long enough wires it seems that the C_{4n+2} chains are likely metal and the hydrogen end-capped HC_{2nH} wires could be semiconductors. The C_{4n+2} rings, with the highest symmetry and completely delocalized π-electrons, could become superconductors.

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