Gas phase electronic spectrum of the nitrogen terminated nanowire NC$_{16}$N

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Abstract

The UV electronic spectrum of NC$_{16}$N has been measured by means of a mass selective resonant two-color two-photon ionization technique. The observed bands are assigned to the dipole allowed, B $^1$R$^+$ Û X$^1$R$^-$, electronic transition. The electronic structures of NC$_{2n}$N ($n = 2$–$8$) in the ground and excited states have been investigated using density functional theory. The calculated transition energies of the A $^1$D$^u$ (!$^1$R$/C^0u$) Û X$^1$R$^+$ and the B $^1$R$^+$ Û X$^1$R$^+$ systems decrease monotonically with increasing chain size and slowly converge to the HOMO–LUMO gap of the long chain limit. The present studies imply that a long carbon nanowire terminated with nitrogen will be semiconducting due to $\pi$-electron localization and bond-length alternation.

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1. Introduction

The development of a variety of experimental methods in recent years has made it possible to produce materials with lower dimensionality than those usually encountered in nature. The properties and electronic structure of, for example, a 1D nanowire, may differ significantly from that of 3D materials and show strong quantum behavior [1]. One-dimensional carbon-based materials like nanotubes [2], Pt-containing polyyne [3], and hydrogen terminated polyyne [4] have become of significant scientific and technological interest. One of the central questions is if the material is a semiconductor with $\pi$-electrons around the Fermi level, and whether the electrons are delocalized over the complete carbon backbone. In our previous publications, the gas phase electronic spectra of hydrogen terminated carbon nanomolecular wires such as HC$_{2n}$H [4,5] and HC$_{2n+1}$H [6] were studied by a mass selective resonant two-color two-photon ionization (R2C2PI) technique in a supersonic molecular beam. For the closed shell even chains HC$_{2n}$H it was found that convergence to bulk behavior was slow and that a significant optical band-gap of 3.3 eV persisted in chains as long as 3 nm (HC$_{26}$H).

Molecular wires likely to find employment in technological applications are modified at their ends such that they may bind covalently to gold electrodes or other materials. An example is the use of the lone-pair bearing nitrogen atom in pyridine as a molecular ‘alligator clip’ [7]. It is therefore of interest to investigate the effects of chemical substitution on the electronic structure of the hydrogen-terminated nanowires studied previously.

In this Letter, the gas phase electronic spectrum of the nitrogen terminated nanowire NC$_{16}$N is presented and analyzed. The results of theoretical calculations using time-dependent density functional theory (TD-DFT) of the band gaps of the nitrogen terminated carbon nanowires are presented and discussed in terms of the electronic structure of these species.

2. Experiment

The experimental set-up has been described in detail elsewhere [8]. It consisted of a molecular beam combined with a linear time of flight mass-analyzer. The source used to produce NC$_{16}$N was a pulsed valve...
coupled to an electric discharge through which a gas mixture comprising 0.5% dicyanoacetylene (NCCCCN) in argon (backing pressure 8 bar) was expanded. A 100–200 μs pulse (600–900 V) was applied between the electrodes resulting in a current of 100 mA. The emerging molecular beam containing the NC16N dicyanopolyyne entered the ionization region through a 2 mm skimmer. Ions were removed prior to the skimmer by an electric field. The neutral molecules were then ionized by the R2C2PI method and the ions extracted towards a detector. The mass resolution of the instrument was ≈900. The ion signal of a large number of masses was simultaneously recorded as a function of the wavelength.

R2C2PI spectra were recorded in the near UV range. The excitation photons were produced by the frequency doubled output of a dye laser (bandwidth ~ 0.1 cm⁻¹) pumped by the second harmonic of a Nd:YAG laser. The ionizing photons at 157 nm were produced by a F₂ excimer laser with the energy of a few mJ/pulse. Both lasers were unfocused. The excitation laser beam was anti-collinear to the molecular beam while the F₂ laser lasers were unfocused. The excitation laser beam was perpendicular to the molecular beam. The temporal sequence of the two lasers was optimized to maximize the R2C2PI signal, the F₂ laser pulse usually passing through the molecular beam a few ns after the dye laser.

The bands observed in the spectrum were due to a 1 + 1’ resonance. This was confirmed by the absence of signal at the appropriate mass-to-charge ratio in the absence of either laser pulse. Transitions from 2 + 1’ resonances were not expected to be seen because the molecular density in the source is low and the small laser power (~10⁷ W cm⁻²) did not favor multiphoton processes.

3. Results and discussion

3.1. Spectroscopy

The observed R2C2PI spectrum of NC16N is shown in Fig. 1. The corresponding transition of the isoelectronic HC18H molecule is reproduced from [6] in the bottom trace. The wavelength maxima of the observed vibronic transitions and the suggested assignments are given in Table 1. Because the spectrum was recorded under the low temperature conditions of a supersonic molecular beam, vibrational hot bands are not expected. The band observed ~209 cm⁻¹ to the blue of the origin is attributed to the excitation of the lowest frequency ς_g transition, which corresponds to a stretching vibrational mode as suggested by ab initio calculation [9]. This value is near identical to the lowest ς_g vibrational frequency of the isoelectronic HC18H molecule (Table 1). The observed vibronic bands of the NC16N chain are due to the dipole-allowed B¹Σ_u⁺ ← X¹Σ_g⁻ electronic transition.

The oscillator strength of the B¹Σ_u⁺ ← X¹Σ_g⁻ system may be calculated using the formula \( f = \frac{2}{3} \Delta E \times |R_{u'v'}|^2 \), where \( \Delta E \) is the vertical transition energy (in Hartree) of the B¹Σ_u⁺ ← X¹Σ_g⁻ transition and \( R_{u'v'} \) is the transition dipole moment (in a.u.). For a single electron, by definition, the sum of all transitions yields a combined oscillator strength of unity. For an N-electron atom, the Thomas–Reiche–Kuhn rule states that the sum of oscillator strengths for all transitions is \( N \) [10]. Static electron correlation, which allows mixing of formal one-electron transitions, is responsible for oscillator strengths of individual transitions greater than unity but not greater than \( N \). In many electron systems, the transition energy and transition moment values are often calculated without sufficiently accounting for the effects of dynamic electron correlation. Also, the basis sets implemented are designed to describe that part of the wavefunction of highest electron density. In the length formalism, the transition dipole moment calculation may suffer from the regions of the wavefunction far from the nuclei being described poorly (yet sufficiently well for calculation of energy). For the HC₂n⁺1H series [6] where the behavior of the oscillator strength was seen to be of great importance to astrophysics, the calculated \( f \)-value for a given (strong) transition was seen to vary by nearly a factor of two between CASSCF and MRCI levels of theory. The errors associated with both the calculated transition energy and transition moment values allow for calculated oscillator strengths much greater than expected. Such calculated values, while overestimated, indicate substantial actual oscillator strengths.

The calculated oscillator strength of the B¹Σ_u⁺ ← X¹Σ_g⁻ transition at the TD-DFT level of theory in the length formalism is ~7. This may be compared to the value of ~9 taken from [9] (ZINDO). It has been shown
that in some cases the value calculated within the gradient (momentum) formalism is more accurate [7]. In this case, the oscillator strength in the momentum formalism is \( \lambda = C_{24}^5 \). It has been suggested that as the formalisms should agree for an accurate wavefunction, a reasonable value can be obtained by taking the geometric mean of the two.

### 3.2. Electronic structure: size dependence of NC\(_{2n}\)N

#### 3.2.1. HOMO–LUMO gap

The \( \Sigma^+ \Sigma_g^- \) ground state electronic configuration of NC\(_{16}\)N is dominated by the configuration \( \ldots |18\sigma_u|^2 |19\sigma_g|^2 |4\pi_g|^4 |5\pi_u|^4 \). The HOMO is 5\( \pi_u \) and the LUMO is 5\( \pi_g \). Calculations of the HOMO–LUMO gap (Fig. 3) were carried out using the GAUSSIAN 98 suite of programs [11] at the hybrid density functional (B3LYP) level of theory [12] with Dunning’s correlation consistent basis sets cc-pVDZ [13] in the optimized ground state geometries taken from [9]. The HOMO–LUMO gap is seen to decrease with increasing chain length, as expected, and the discrepancy between this value and the observed transition energies is seen to decrease (Fig. 4).

#### 3.2.2. Band gaps

Calculations of vertical electronic excitation energies (band gaps) were undertaken using TD-DFT [14]. To a first approximation, the \( \Sigma_u^+ \) and \( \Delta_u \) states of NC\(_{16}\)N, arise from the same configuration produced by excitation from 5\( \pi_u(x,y) \) to 5\( \pi_g(y,x) \). Excitation from 5\( \pi_u(x,y) \) to 5\( \pi_g(x,y) \) results in the \( \Sigma_u^+ \) excited state. The \( \Sigma_u^+ \) state corresponds to 5\( \pi_u \) to 19\( \sigma_g \) electron promotion. The calculated band gaps, \( \Delta_{A-X}, \Delta_{B-X} \) and

![Fig. 2. The wavelength of the origin band in the \( \Sigma_u^+ \Sigma_g^- \) transitions observed experimentally here and in [15], and predicted by TD-DFT theory and the free-electron model (FEM) as function of the length of carbon chains NC\(_{2n}\)N (\( n = 2–8 \)) size.](image)

<table>
<thead>
<tr>
<th>( \lambda ) (nm)</th>
<th>( v ) (cm(^{-1} ))</th>
<th>( \Delta v ) (cm(^{-1} ))</th>
<th>Assignment</th>
<th>( T_0 )(observed) (eV)</th>
<th>( T_0 )(calculated) (eV)</th>
<th>( f_{cal} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>NC(_{16})N</td>
<td>286.4</td>
<td>34906(5)</td>
<td>0.0</td>
<td>0( |^1 )</td>
<td>4.33</td>
<td>3.717</td>
</tr>
<tr>
<td></td>
<td>284.5</td>
<td>35115(5)</td>
<td>209(5)</td>
<td>( \nu(\sigma_g^+ )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HC(_{18})H</td>
<td>295.9</td>
<td>33784(5)</td>
<td>0.0</td>
<td>0( |^2 )</td>
<td>4.18</td>
<td>3.480</td>
</tr>
<tr>
<td></td>
<td>294.1</td>
<td>33994(5)</td>
<td>210(5)</td>
<td>( \nu(\sigma_g^+ )</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1 Observed band maxima in the \( \Sigma_u^+ \Sigma_g^- \) electronic transition of NC\(_{16}\)N and HC\(_{18}\)H

![Fig. 3. An MO description of the electronic ground states of NC\(_{2n}\)N and HC\(_{2n+2}\)H. \( \lambda \) is the projection of orbital angular momentum onto the molecular axis. The Fermi level is indicated by the dotted line.](image)

![Fig. 4. The calculated HOMO–LUMO gap and the bands gaps \( \Delta \) (electronic transition energies) as the function of the length of carbon chains NC\(_{2n}\)N (\( n = 2–8 \)).](image)
$\Delta_{C-X}$, are shown in Fig. 4 as a function of the size of the carbon chains.

The band gaps $\Delta_{A-X}$ and $\Delta_{B-X}$ decrease with increasing chain size and should converge to $\Delta_{\text{HOMO-LUMO}}$ in the limit of long chains. However, the plots in Fig. 4 show that the convergence is very slow, as observed for the hydrogenated chains [4]. The chain NC$_{16}$N ($\sim$2 nm in length) is still far away from exhibiting bulk properties. In contrast, the band gap $\Delta_{C-X}$ converges to the IP of the chain rather than to $\Delta_{\text{HOMO-LUMO}}$. This is probably due to the electronic state $C^1\Pi_u$ being Rydberg in character as is the case for NC$_4$N [15].

For bare C$_{2n}$ chains the bonding structures in the ground state were predicted to be of the cumulene type [16]. The calculated bond length alternation [9] in the ground state for the nitrogen terminated carbon chains highlights the important role of the end-capped nitrogen atoms. It has been pointed out that the very slow convergence to bulk is due to the slow decay of the bond length alternation induced by the symmetry and quantum effects of the terminal atoms [4]. Bond length alternation between single and triple carbon–carbon bonds is due to $\pi$-electron localization [5]. Ab initio calculations show that the alternation in the ground state of HC$_{2n}$H is more pronounced compared to that in excited state; in the latter, a cumulenic-like carbon skeleton is favored [8]. For example, the calculations for HC$_6$H indicate that the ratios of $R_{C-C}/R_{C=C}$ are $1.3873 \text{ Å}$ for the $\chi^1\Sigma^+_u$ ground state, $1.2860 \text{ Å}$ for the $A^1\Sigma^+_u$ state and $1.3217 \text{ Å}$ for the $B^1\Sigma^+_u$ state, respectively. The structure changes from acetylene-like in the ground state to cumulene-like in the electronic excited states have been experimentally demonstrated by the observed dominant progression involving the C≡C stretch vibrational motion in the $B^1\Sigma^+_u \rightarrow \chi^1\Sigma^+_u$ transition system (see Fig. 2 of [5]). Other theoretical studies have also revealed that the hypothetical infinite polyyne would have a structure of alternating shorter (triple) and longer (single) bonds in the ground state, and would be a semiconductor with orbitals of $\pi$ symmetry around the Fermi level [17]. Experimental evidence for the alternation is found in the plot of the wavelengths of the origin bands of the $B^1\Sigma^+_u \rightarrow \chi^1\Sigma^+_u$ transitions against the number of carbon atoms. This is not exactly linear as predicted by the free electron model (FEM, complete delocalization of $\pi$-electrons). The wavelength seemingly converges to a finite value in the long chain limit due to $\pi$-electron localization (Fig. 2). The similarity between the NC$_{2n}$N and HC$_{2n}$H series (see Fig. 3 of [5]) indicates that the dicyanopolyne nanowires in the ground state are semiconductors but could exhibit metallic characteristics in the excited electronic state.

4. Conclusion

The gas-phase $B^1\Sigma^+_u \rightarrow \chi^1\Sigma^+_u$ electronic spectrum of NC$_{18}$N has been observed in a supersonic molecular beam. The $0^0_0$ band position and nearby vibrational structure was observed to be extremely similar to the isoelectronic HC$_{18}$H molecule, indicating comparable electronic structure.

The electronic excited states of these chains were also calculated using time-dependent density-functional theory. The slow convergence of the band gap highlighted the important role of the end-capped nitrogen atoms which induce localization of the $\pi$-electrons in the ground state configuration, effectively the same as the effect of –CH termination. The present studies indicate that a long carbon nanowire terminated with nitrogen should be a semiconductor in the ground state but exhibit metallic properties in the excited electronic states due to enhanced $\pi$-electron delocalization.

Acknowledgements

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References