

Size Dependence of Electronic Excitation Energy in Linear $C_{2n}H$ and $C_{2n-1}N^*$

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The geometries, bondings, and vibrational frequencies of $C_{2n}H$ ($n = 3-9$) and $C_{2n-1}N$ ($n = 3-9$) were investigated by means of density functional theory (DFT). The vertical excitation energies for the $X^2\Pi \rightarrow 2^2\Pi$ transitions of $C_{2n}H$ ($n = 3-9$) and for the $X^2\Sigma \rightarrow 2^2\Pi$ and the $X^2\Pi \rightarrow 2^2\Pi$ transitions of $C_{2n-1}N$ ($n = 3-9$) have been calculated by the time-dependent density functional theory (TD-DFT) approach. On the basis of present calculations, the explicit expression for the wavelengths of the excitation energies in linear carbon chains is suggested, namely, $\lambda_0 = [1240.6A / (2 + \frac{3n+6}{3n+3})] (1 - Be^{-Cn})$, where $A = 3.24463$, $B = 0.90742$, and $C = 0.07862$ for $C_{2n}H$, and $A = 2.94714$, $B = 0.83929$, and $C = 0.08539$ for $C_{2n-1}N$. In consideration of a comparison of the theory with the experiment, both the expressions are modified as $\lambda_1 = 0.92(\lambda_0 + 100)$ and $\lambda_1 = 0.95(\lambda_0 + 90)$ for $C_{2n}H$ and $C_{2n-1}N$, respectively.

Keywords DFT and TD-DFT, $C_{2n}H$, $C_{2n-1}N$, Electronic spectrum

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Introduction

Carbon chains are among the most attractive candidates as the carriers of the diffuse interstellar bands (DIBs)^[1]. To detect the carbon chains in dark clouds and carbon stars^[2], it is very important to understand their electronic spectra. Maier and his coworkers have measured the polyacetylenic radicals $C_{2n}H$ ($n = 1-4$) and $C_{2n-1}H$ ($n = 2-6$) by the rotational spectroscopy^[3,4] and the species $n = 4$ have been detected in dark interstellar clouds^[5,6]. In neon matrices, the $B^2\Pi \rightarrow X^2\Pi$ transitions of $C_{2n}H$ ($n = 3-8$)^[7] have been identified by using the mass selection technique. In recent gas phase measurements, the electronic absorption spectra of C_6H ^[8], C_8H and $C_{10}H$ ^[9] were determined by means of the cavity ring down absorption spectroscopy.

Via using the coupled cluster method RCCSD (T) with correlation-consistent valence and core-valence basis sets, the two lowest electronic states $2^2\Pi$ and $2^2\Sigma^+$ of linear carbon chain radicals C_nH ($n = 2-7$) have been investigated, and a $2^2\Pi \rightarrow 2^2\Sigma^+$ state separation of 72 cm^{-1} in energy has been found^[10]. On the basis of the UHF optimized geometries, Sobolewski and Adamowicz^[11] characterized the

electronically excited states of C_4H , C_6H and C_8H by CASPT2/DZVP calculations. Based on the location of the $B^2\Pi \rightarrow A^2\Pi$ transition of C_4H determined with *ab initio* method, an extrapolation with a semiempirical model for the $2^2\Pi \rightarrow X^2\Pi$ transitions of $C_{2n}H$ ($n = 3-6$) is presented^[12].

$C_{2n-1}N$ chains, like isoelectronic $C_{2n}H$, are interesting in connection with the DIBs and the theory. In recent observations of C_5N in the laboratory^[13] and in an astronomical source^[14], the ground state of it is characterized to be a $2^2\Sigma$ symmetry, as predicted by means of the theory^[15]. Longer chains $C_{2n-1}N$ ($n > 2$) are expected to have $2^2\Pi$ ground states^[16,17]. The $B^2\Pi \rightarrow X^2\Pi$ transitions of $C_{2n-1}N$ ($n = 5-7$) were measured in neon matrices at 6 K by Maier and coworkers^[18]. The $B^2\Pi \rightarrow X^2\Pi$ transitions of $C_{2n-1}N$ have similar spectral features in comparison with those of isoelectronic $C_{2n}H$ radicals but they appear at slightly higher energies. At the B3LYP/cc-pVTZ level, the structures and the energetics of carbon-nitrogen clusters with up to 12 atoms have been studied^[19], and $C_{2n-1}N$ chains are predicted to have polyacetylenic structures. The theoretical calculations of other conformations of

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0. 11688	0. 12207	0. 12183 *						
0. 11749	0. 12451	0. 12960						
N—C—C—C—C—C								
0. 13644	0. 13590							
0. 13493	0. 13186							
0. 11696	0. 12242	0. 12264	0. 12202 *					
0. 11727	0. 12370	0. 12555	0. 12951					
N—C—C—C—C—C—C—C								
0. 13620	0. 13480	0. 13553						
0. 13542	0. 13230	0. 13105						
0. 11716	0. 12328	0. 12477	0. 12598	0. 12941				
N—C—C—C—C—C—C—C—C—C								
0. 13594	0. 13392	0. 13303	0. 13324					
0. 11710	0. 12305	0. 12430	0. 12531	0. 12621	0. 12399			
N—C—C—C—C—C—C—C—C—C—C—C—C								
0. 13581	0. 13343	0. 13204	0. 13086	0. 13060				
0. 11708	0. 12294	0. 12403	0. 12487	0. 12566	0. 12636	0. 12927		
N—C—C—C—C—C—C—C—C—C—C—C—C—C								
0. 13587	0. 13364	0. 13274	0. 13146	0. 13054	0. 13051			
0. 11706	0. 12286	0. 12384	0. 12453	0. 12419	0. 12585	0. 12644	0. 12922	
N—C—C—C—C—C—C—C—C—C—C—C—C—C—C—C								
0. 13591	0. 13380	0. 13279	0. 13196	0. 13114	0. 13036	0. 13046		
0. 11705	0. 12281	0. 12371	0. 12429	0. 12483	0. 12540	0. 12599	0. 12650	0. 12918
N—C—C—C—C—C—C—C—C—C—C—C—C—C—C—C—C—C								
0. 13594	0. 13392	0. 13303	0. 13234	0. 13166	0. 13093	0. 13024	0. 13042	

Fig. 2 The B3LYP optimized geometries of $C_{2n+1}N$.

* Indicating the geometries of ${}^2\Sigma$.

Table 1 The vibrational frequencies of $C_{2n}H$ ($n=3-9$) by B3LYP approach*

Species	Vibrational frequencies* / cm^{-1}
C_6H	1905(218), 2110(24), 2147(202), 3482(119)
C_8H	1917(294), 2077(80), 2122(120), 2211(443), 3483(160)
$C_{10}H$	1918(417), 2109(287), 2189(780), 2220(336), 3485(204)
$C_{12}H$	1902(268), 1930(309), 2096(216), 2167(1590), 2194(354), 3486(251)
$C_{14}H$	1922(608), 2085(431), 2150(290), 2158(2077), 2219(367), 3487(292)
$C_{16}H$	1788(142), 1921(694), 2076(242), 2110(2917), 2143(82), 2196(977), 2225(129), 3487(325)
$C_{18}H$	1733(187), 1919(791), 2067(1615), 2077(1967), 2128(634), 2187(581), 2199(841), 2233(214), 3488(362)

* The bold data indicating C—H stretching mode; italic data indicating C—C stretch mode.

Table 2 The vibrational frequencies of $C_{2n-1}N$ ($n=3-9$) by B3LYP approach*

Species	Vibrational frequencies* / cm^{-1}
C_5N	1215(12) , 1915(213), 2126(123), 2226(27)
C_7N	1317(22) , 1915(270), 2054(237), 2164(252), 2282(18)
C_9N	1461(30) , 1914(205), 1966(401), 2141(448), 2207(292), 2302(14)
$C_{11}N$	1516(32) , 1927(704), 2121(416), 2187(838), 2216(31), 2314(102)
$C_{13}N$	1554(50) , 1811(181), 1919(652), 2103(401), 2155(1079), 2187(525), 2237(257), 2321(127)
$C_{15}N$	1581(112) , 1667(276), 1920(803), 2095(575), 2168(394), 2211(1157), 2243(173), 2325(157)
$C_{17}N$	1598(46) , 1714(190), 1917(840), 2079(564), 2085(787), 2153(702), 2199(2078), 2214(45), 2330(190)

* The bold data indicating the C—C stretch mode; italic data indicating C—C, C—N stretch mode.

(T) levels, the energy difference was found to be 0.588 and -2.268 kJ/mol, respectively. Using

large-scale RCCSD(T) calculations, Botschwina^[15] predicted that the ${}^2\Sigma$ state is more stable than the ${}^2\Pi$ state by about 500 cm^{-1} .

The selected strong vibrational frequencies and their IR intensities of $C_{2n}H$ and $C_{2n-1}N$ are presented in Tables 1 and 2, respectively. The C—H stretching frequency is almost unchanged at 3485 cm^{-1} , while the corresponding intensity increases with the chain size. A comparison of the calculated C—C stretching frequencies with available experimental values shows a good agreement between the theory and the experiment. For example, the B3LYP calculation indicates the C—C stretching frequency to be 1917 cm^{-1} in C_8H , reasonably close to the experimental value of 2080 cm^{-1} [7].

2 Electronic Transitions of $C_{2n}H$

$C_{2n}H$ species have an electronic configuration of $\dots(\sigma)^2(\pi)^4(\pi)^3$, and the π - π electron excitations give rise to low-lying ${}^2\Pi$ states. The vertical transition energies and the oscillator strengths determined by the TD-B3LYP calculations for the ${}^2\Pi$ $X^2\Pi$ transitions of $C_{2n}H$ ($n=3-9$) are listed in Table 3. A comparison of the calculated transition energies and the observed values in Table 3 shows that the TD-B3LYP calculations systematically overestimate the vertical transition energies by about 50 nm for the small chains. The calculated wavelength differences between the adjoining bands for the ${}^2\Pi$ $X^2\Pi$ transitions of $C_{2n}H$ ($n=3-9$) in Table 3 are 99.12, 93.33, 87.35, 82.41, 75.79, and 68.92 nm, respectively, as n increases

from 3 to 9, showing a slightly nonlinear λ - n dependence. The nonlinearity has been observed experimentally for $C_{2n}H$ species with $n=3-8$ ^[7].

Table 3 Vertical transition energies (nm) and oscillator strengths (f) for $X^2\Pi$ \rightarrow $^2\Pi$ of $C_{2n}H$ ($n=3-9$)

n	$\lambda_{\text{calc.}} / \text{nm}$	$\lambda_{\text{expt.}}^{[7]} / \text{nm}$	Transition	f
3	473.71	530	$2\Pi \rightarrow 3\Pi$	0.0250
4	572.83	631	$3\Pi \rightarrow 4\Pi$	0.0311
5	666.16	722	$4\Pi \rightarrow 5\Pi$	0.0371
6	753.51	801	$5\Pi \rightarrow 6\Pi$	0.0439
7	835.92	866	$6\Pi \rightarrow 7\Pi$	0.0516
8	911.71	924	$7\Pi \rightarrow 8\Pi$	0.0613
9	980.63		$8\Pi \rightarrow 9\Pi$	0.0714

In valence bond theory, Li and Paldus^[22] suggested an explicit expression for the excitation energy of linear polyenes $C_{2n}H_{2n+2}$, *i. e.*,

$$\Delta E = 1 + (1/2) \left(\frac{1}{3n+6} - \frac{1}{3n+3} \right)$$

(in units of the exchange parameter of Heisenberg Hamiltonian). Considering two sets of extended π orbital series in carbon chains $C_{2n}H$ and $C_{2n-1}N$ instead of one π MO series in $C_{2n}H_{2n+2}$, we introduced a factor A into the initial excitation energy formula. Furthermore, an exponential term was incorporated into the wavelength expression to account for the nonlinear behavior of the excitation energies. The predicted wavelength (in nm) of the band origin for the $^2\Pi \rightarrow X^2\Pi$ transitions in $C_{2n}H$ is given by

$$\lambda_0 = \frac{1240.6A}{2 + \frac{1}{3n+6} - \frac{1}{3n+3}} (1 - Be^{-Cn}) \quad (1)$$

where $A = 3.24463$, $B = 0.90742$ and $C = 0.07862$; $1240.6 = hc$, h is the Planck constant and c is the light velocity. Combining the experimental data with theoretical results, we have a modified formula

$$\lambda_1 = 0.92(\lambda_0 + 100) \quad (2)$$

3 Electronic Transitions of $C_{2n-1}N$

Vertical transition energies and oscillator strengths determined by TD-B3LYP calculations for $^2\Pi \rightarrow X^2\Pi$ and $^2\Pi \rightarrow X^2\Sigma$ transitions in $C_{2n-1}N$ ($n=3-9$) are listed in Table 4. A comparison of the calculated transition energies with the observed values given in Table 4 shows that TD-B3LYP calculations generally overestimate the transition energies by 30–50 nm. The calculated wavelength differences between the adjoining bands of $^2\Pi \rightarrow X^2\Pi$ transitions in $C_{2n-1}N$ ($n=5-9$) in Table 4 are 83.49, 78.55, 72.28, and 66.06 nm, respectively, showing a nonlinear λ - n relationship as in the

case of isoelectronic $C_{2n}H$. Such a nonlinearity of the size dependence of the wavelength has been observed experimentally for the species with $n=5-7$ ^[18].

Table 4 Vertical transition energies (nm) and oscillator strengths (f) for $X^2\Sigma$ \rightarrow $^2\Pi$ of $C_{2n-1}N$ ($n=3, 4$) and $X^2\Pi$ \rightarrow $^2\Pi$ of $C_{2n-1}N$ ($n=3-9$)

n	State	$\lambda_{\text{calc.}} / \text{nm}$	$\lambda_{\text{expt.}}^{[18]} / \text{nm}$	Transition	f
3	$X^2\Sigma \rightarrow ^2\Pi$	439.24	470.4	$2\Pi \rightarrow 12\sigma$	0.0004
	$X^2\Pi \rightarrow ^2\Pi$	441.67		$2\Pi \rightarrow 3\Pi$	0.0202
4	$X^2\Sigma \rightarrow ^2\Pi$	561.43	581.9	$3\Pi \rightarrow 17\sigma$	0.0004
	$X^2\Pi \rightarrow ^2\Pi$	533.94		$3\Pi \rightarrow 4\Pi$	0.0218
5	$X^2\Pi \rightarrow ^2\Pi$	622.87	675.6	$4\Pi \rightarrow 5\Pi$	0.0246
6	$X^2\Pi \rightarrow ^2\Pi$	706.36	757.2	$5\Pi \rightarrow 6\Pi$	0.0285
7	$X^2\Pi \rightarrow ^2\Pi$	784.91	827.5	$6\Pi \rightarrow 7\Pi$	0.0329
8	$X^2\Pi \rightarrow ^2\Pi$	857.19		$7\Pi \rightarrow 8\Pi$	0.0386
9	$X^2\Pi \rightarrow ^2\Pi$	923.25		$8\Pi \rightarrow 9\Pi$	0.0451

Like $C_{2n}H$, the predicted wavelength (in nm) of the $^2\Pi \rightarrow X^2\Pi$ transitions in $C_{2n-1}N$ is also expressed as

$$\lambda_0 = \frac{1240.6A}{2 + \frac{1}{3n+6} - \frac{1}{3n+3}} (1 - Be^{-Cn}) \quad (3)$$

where $A = 2.94714$, $B = 0.83929$ and $C = 0.08539$; $1240.6 = hc$, h is the Planck constant and c is the light velocity. Combining the experimental data with the theoretical results, we have an improved formula

$$\lambda_1 = 0.95(\lambda_0 + 90) \quad (4)$$

Interestingly, it is noted that the parameters B and C in eq. (3) are almost the same as those in eq. (1), even there is a notable difference for the linear parameter A . This shows that there is a similar bonding for isoelectronic species $C_{2n}H$ and $C_{2n-1}N$.

Conclusion

The geometries and the frequencies of $C_{2n}H$ ($n=3-9$) and $C_{2n-1}N$ ($n=3-9$) have been determined by B3LYP calculations. The current calculations reveal that both the series have dominant acetylenic structures, whereas the terminals without any H or N atom approach cumulenic structures as the chain increases.

On the basis of the present calculations and available experimental data, the size dependences of the excitation energies of linear carbon chains $C_{2n}H$ and $C_{2n-1}N$ are quantitatively reproduced with explicit analytical expressions. The slightly nonlinear dependence of the wavelength of the $^2\Pi \rightarrow X^2\Pi$ transition on the chain size is discussed for isoelectronic $C_{2n}H$ and $C_{2n-1}N$, which results in con-

vergent wavelengths of 1943. 6 and 1822. 2 nm for enough long $C_{2n}H$ and $C_{2n-1}N$ chains, respectively.

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