Structure and Electronic Spectrum of Linear Carbon Chain $PC_{2n}P$ Studied with DFT

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Abstract: The geometries and the vibrational frequencies of linear carbon chain $PC_{2n}P$ ($n=1-10$) were investigated by density functional theory (DFT) at the B3LYP/6-31G** and B3LYP/6-311G** levels. Time-dependent density functional theory (TD-DFT) was employed to calculate the vertical transition energies and oscillator strengths. On the basis of present calculations, the explicit expressions for the size dependence of the excitation energy in linear carbon chain was suggested.

Keywords: linear chain $PC_{2n}P$; DFT; TD-DFT; electronic spectra; analytic expression

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线型碳链 $PC_{2n}P$的结构和电子光谱的密度泛函理论研究

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摘 要: 应用密度泛函理论, 在 B3LYP/6-31G** 和 B3LYP/6-311G** 水平上优化得到了线型簇合物 $PC_{2n}P$($n=1-10$)的基态平衡几何构型, 计算了它们的谐振动频率. 在基态平衡构型下, 利用含时密度泛函理论, 计算得到了簇合物 $PC_{2n}P$($n=1-10$)的垂直激发能和相应的振子强度, 导出了激发能与体系大小 n 的解析关系式.

关键词: 线型碳链 $PC_{2n}P$; 密度泛函理论; 含时密度泛函理论; 电子光谱; 解析表达式

Carbon-chain species are widely present in the interstellar medium as possible carriers of the diffuse interstellar bands (DIBs). They play an important role in the chemistry of the diffuse interstellar medium as well as their extraordinary electrical properties. Because of their high reactivity, bare carbon chains are readily terminated by a wide variety of atoms to form XC_n or XC_nX linear clusters, which were summarized by Burnin and Bel-Bruno[1]. The linear phosphaalkynes HC_3P was first detected by Kroto and co-workers by microwave spectroscopy in the pyrolysis products of a gaseous mixture of propargyl chloride and phosphorus trichloride, from which a large amount of rotational data are presently available[2-5]. Phosphahexatriyne (HC_5P) has also been detected in the pyrolysis products of PCl_3 and toluene mixtures[6]. In this paper, we calculate the structures, vibrational frequencies and electronic spectra of linear polyynes $PC_{2n}P$ ($n=1-10$) by DFT and TD-DFT. The stable structures are obtained. The size dependence of the excitation energy in linear chain has been explored.

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1 Computational Details

The equilibrium geometries and vibrational frequencies of the polyynes $PC_{2n}P$ in their ground states were determined by the B3LYP functional calculations with the standard 6-31G** and 6-311G** basis sets as implemented by the GAUSSIAN 98 program package. Vertical excitation energies of the $X\ ^1\Sigma_g^+ \rightarrow 1\ ^1\Sigma_u^+$ transitions in $PC_{2n}P$ were calculated by the time-dependent density-functional response theory (TD-B3LYP) with the cc-pvTZ ($n=1-6$) and cc-pvDZ ($n=1-10$) basis sets at B3LYP/6-31G** optimised geometries.

2 Results and Discussion

2.1 Optimized Geomitries and Vibrational Frequencies

The optimized bond lengths of linear carbon chain $PC_{2n}P$ are displayed in Fig. 1. As Fig. 1 displays, $PC_{2n}P$ has a bond-length alternation between single and triple bonds, showing the structure as P≡C—C≡C…C—C≡P.

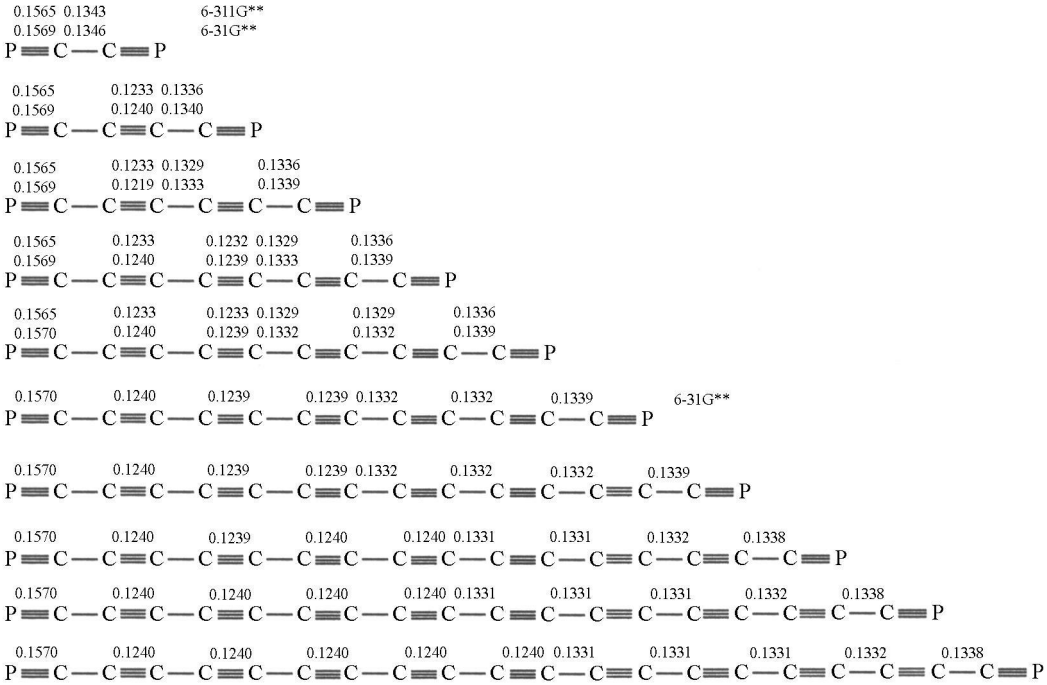

Fig. 1 The B3LYP optimized bond Length (nm) of $PC_{2n}P$ ($n=1-10$)

For such clusters, the optimized C≡P bond length is in the range of 0.1569 nm ~0.1570 nm, and the bond length of C≡C is in the range of 0.1239 nm ~0.1240 nm. For the same molecule, the bond length of C—C decreases along the chain from the terminal to the middle, but that of C≡C is almost unchanged. All the vibrational frequencies obtained are real, which shows that these linear clusters correspond to energy minima on the potential energy surface. For such clusters, the available information is very scarce. Computation results show the bending frequencies of $PC_{2n}P$ are very small (179.5, 84.3, 49.7, 33.2, 23.8, 17.9, 14.0, 11.3, 9.4, 8.3 cm^{-1}, respectively, for $n=1-10$). It indicates that these linear clusters are very floppy. Interestingly, the symmetric stretching frequencies of C—C next to C≡P change regularly: as n is odd, the frequencies decrease; as n is even, the frequencies increase with n increases.

2.2 Vertical Transition Energies

Table 1 presents the vertical transition energies and oscillator strengths for the transition $X\ ^1\Sigma_g^+ \rightarrow 1\ ^1\Sigma_u^+$ in $PC_{2n}P$ which were determined by the TD-B3LYP/cc-pvTZ ($n=1-6$) and TD-B3LYP/cc-pvDZ ($n=1-10$) calculations.

Computation results reveal that all the promotions are from π_g to π_u (odd-n) or from π_u to π_g (even-n). It can

be seen that as n increases, the vertical transition energies decrease gradually, while the intensities increase. The plot of the λ-n relationship for $PC_{2n}P$ is shown in Fig. 2.

Table 1　Vertical transition energies and oscillator strengths(f) of $X\ ^1\Sigma_g^+ \rightarrow 1^1\Sigma_u^+$ transition for $PC_{2n}P$

n	transition	λ[a](λ[b]) /nm	f[a](f[b])
1	$2\pi_g \rightarrow 3\pi_u$	214.62(222.50)	1.7327(1.7151)
2	$3\pi_u \rightarrow 3\pi_g$	242.00(249.37)	2.9893(2.9542)
3	$3\pi_g \rightarrow 4\pi_u$	270.55(277.37)	4.0491(4.0207)
4	$4\pi_u \rightarrow 4\pi_g$	299.03(305.49)	4.9301(4.9174)
5	$4\pi_g \rightarrow 5\pi_u$	326.86(332.98)	5.6701(5.6791)
6	$5\pi_u \rightarrow 5\pi_g$	353.78(359.62)	6.3149(6.3411)
7	$5\pi_g \rightarrow 6\pi_u$	379.60	6.8979
8	$6\pi_u \rightarrow 6\pi_g$	404.24	7.4439
9	$6\pi_g \rightarrow 7\pi_u$	427.77	7.9858
10	$7\pi_u \rightarrow 7\pi_g$	450.12	8.4903

[a] by TD-B3LYP/cc-pvDZ　[b] by TD-B3LYP/cc-pvTZ

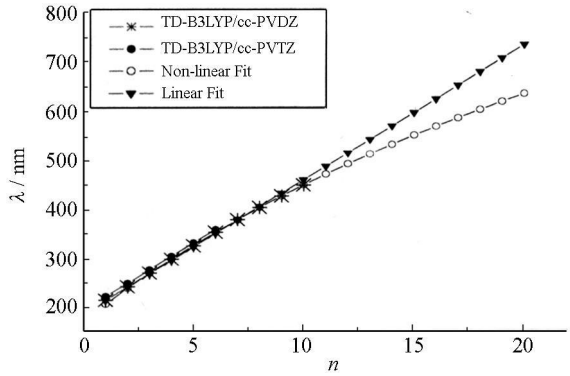

Fig. 2　Plot of the wavelength of the $X\ ^1\Sigma_g^+ \rightarrow 1^1\Sigma_u^+$ electronic transition *vs* n

It is evident that the nonlinear fitting curve and calculated curve coincide with each other very well, so we predict λ-n is nonlinear. Unfortunately, we haven't found the experimental values.

On the basis of the expression $\triangle E=[1+(1/2)(\sqrt{3n+6}-\sqrt{3n+3})]J$ suggested by Li and Pallus[7], we introduce the parametric wavelength (in nm)

$$\lambda = \frac{1\,240.6}{2+\sqrt{3n+6}-\sqrt{3n+3}}(A-BC^n) \qquad (1)$$

where $1\,240.6=hc$, h is Planck constant and c is the light velocity. By fitting the calculated wavelengths of $PC_{2n}P$ ($n=3-10$), the parameters A, B and C are determined, *i.e.*, $A=1.753\,34$, $B=1.381\,54$, and $C=1.039\,86$. From the wavelength expression (1), λ monotonously increases with the increasing chain size, and as $n\rightarrow\infty$, λ approaches to a limit value of 1 087.6 nm.

Conclusions: Present computations reveal a triple and single bond alternation structure for the ground states of linear chain $PC_{2n}P$. Based on current calculations, the size dependence of the excitation energy in linear cluster is quantitatively reproduced with explicit analytical expressions. Linear cluster $PC_{2n}P$ shows λ-n nonlinear dependence. As the chain length increases to infinite, the wavelength will converge to the limit value of 1 087.6 nm.

References:

[1] Burmin A, Bel'Bruno J J. SC_nS linear chain production by direct laser ablation[J]. *J Phy Chem A*, 2003, 107: 9547-9553.

[2] Kroto H W, Nixon J F, Ohno K. The microwave spectrum of phosphabutadiyne, H—C≡C—C≡P[J]. *J Mol Spectrosc*, 1981, 90: 512-516.

[3] Bizzocchi L, Degli E C, Botschwina P. Millimeter wave spectroscopy of HC_3P isotopomers and coupled cluster calculations: the molecular structure of phosphabutadiyne[J]. *Chem Phys Lett*, 2000, 319: 411-417.

[4] Bizzocchi L, Thorwirth S, Müller H S P, *et al*. Submillimeter wave spectroscopy of phosphaalkynes, HCCCP, NCCP, HCP, and DCP[J]. *J Mol Spectrosc*, 2001, 205: 110-116.

[5] Bizzocchi L, Degli E C, Dore L, *et al*. Millimeter wave spectroscopy of HCCCP in excited vibrational states[J]. *J Mol Spectrosc*, 2001, 205: 164-172.

[6] Bizzocchi L, Degli E C, Botschwina P. Millimeter wave spectroscopy and coupled cluster calculations for a new phosphorus carbon chain, HC_5P[J]. *J Chem Phys*, 2003, 119: 170-175.

[7] Li X Z, Pallus J. Size dependence of the $X\ ^1A_g \rightarrow 1^1B_u$ excitation energy in linear polyenes[J]. *Inter J Quant Chem*, 1999, 74: 177-192.