

Gas Phase $1^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$ Electronic Spectra of Polyacetylenes HC_{2n}H , $n = 5-7^\dagger$

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The $1^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$ system in polyacetylenes HC_{2n}H ($n = 5-7$) has been observed for the first time in the gas phase. The UV absorption spectra of these chains were recorded using the resonant two-color two-photon ionization technique. A strong vibrational progression corresponding to the acetylenic stretching mode in the excited state has been observed. The absorption energy showed an inverse dependence on the chain length. The relaxation process of the $1^1\Sigma_u^+$ excited state has been discussed.

The atmosphere of Saturn's moon, Titan, is mainly composed of N_2 and CH_4 .¹⁻³ The complex chemistry initiated by the photolysis of these gases has attracted substantial interest in the last two decades.⁴⁻⁶ Titan is the only other object in the solar system with an atmosphere resembling that of the early earth. This similarity has intrigued scientists to better understand the chemical processes that eventually led to the origin of life on earth.⁷ The other interesting feature of Titan is the thick organic haze layer that appears as an orange fog obscuring its surface. Several photochemical models⁸⁻¹⁰ have been developed to gain insight into the various pathways leading to the formation of haze particles. It has been understood that these aerosol particles are the end products of the aggregation of small molecules such as, C_2H_2 , C_2H_4 , C_4H_2 , C_6H_6 , and HCN , which have been detected on Titan. Polyacetylenes, cyanopolyacetylenes, and polycyclic aromatic hydrocarbons are considered as precursors to the formation of aerosols. In the case of polyacetylenes, which is the focus of this article, C_4H_2 is the only member to be detected on Titan thus far. However, the presence of longer members cannot be ruled out. In terms of laboratory measurements, UV absorption spectra of known polyyenes have been helpful in obtaining absorption cross sections, which were then used to calculate photolysis rates and deduce relative abundances of longer members in the series.¹¹

In this Article we present the electronic spectra corresponding to the $1^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$ band system in the polyacetylene chains HC_{10}H , HC_{12}H , and HC_{14}H , observed for the first time in the gas phase. The spectra were recorded using the resonant two-color two-photon ionization (R2C2PI) technique. Gas phase studies of the above band system in the lower and higher homologues HC_{2n}H ($n = 1-4$)¹² and HC_{2n}H ($n = 8-13$)¹³ are available. They have also been measured in solution ($n = 5-10$, 12)¹⁴ and in neon matrices ($n = 6-12$).¹⁵ However, for $n = 5$, 6, and 7 only the forbidden $A^1\Delta_u \leftarrow X^1\Sigma_g^+$ band system has been observed thus far in the gas phase.¹⁶

Details of the experimental setup can be found in a previous publication.¹⁷ In brief, an electric discharge of a gas mixture pulse (1% diacetylene in He) followed by supersonic expansion into vacuum produced HC_{2n}H in sufficient yield. The contents of the jet-cooled molecular beam were collimated by a 2 mm skimmer and allowed to enter the extraction region of a pulsed time-of-flight mass spectrometer. The R2C2PI spectroscopy was performed by sequentially exposing the molecular beam to the output of a tunable OPO ($\sim 5\text{ cm}^{-1}$ bandwidth) and subsequently to an F_2 (157 nm) excimer laser. The resulting ions were

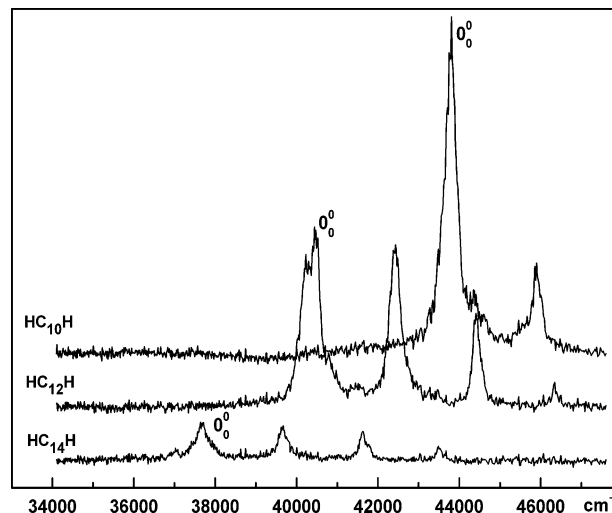


Figure 1. $1^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$ electronic absorption band system of polyacetylenes, HC_{2n}H ($n = 5-7$).

extracted in a two stage acceleration setup and detected using a microchannel plate detector. Excited state lifetimes were measured by recording the ion signal as a function of the delay between the excitation and ionization lasers and fitting resulting decay curves to an exponential function.

The even membered polyacetylenes, HC_{2n}H , are closed shell species with a $1^1\Sigma_g^+$ ground state, which is derived from either a π_g^4 or a π_u^4 electronic configuration. Promotion of an electron $\pi_g \rightarrow \pi_u^*$ or $\pi_u \rightarrow \pi_g^*$ gives rise to the $1^3\Sigma_u^+$, $1^3\Sigma_u^-$, and $1^3\Delta_u$ excited states. According to the dipole selection rules, a $1^1\Sigma_u^+$ excited state can be accessed from a $1^1\Sigma_g^+$ ground state and will therefore carry most of the oscillator strength. Figure 1 displays the electronic spectra assigned to the $1^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$ transition in linear polyacetylenes, HC_{2n}H ($n = 5, 6$ and 7). Each spectrum is dominated by a strong vibrational progression corresponding to the excitation of the $-\text{C}\equiv\text{C}-$ stretching mode in the excited state. Table 1 provides a list of the band positions along with the known experimental (neon matrix and solution)^{14,15} and theoretical¹⁸ absorption wavelength of this band system.

As seen in Figure 1, the $1^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$ band system shifts to the red with increasing chain length. Previous studies have shown that a plot of the wavelength vs the number of carbon atoms, exhibits a sublinear dependence.¹³ This has been attributed to the localization of the π electron cloud in linear polyyenes. DFT calculations on the $1^1\Sigma_g^+$ ground state have shown that these molecules possess a linear geometry and exhibit a

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TABLE 1: Observed Band Positions in the ${}^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$ Electronic Transition of HC_{2n}H ($n = 5-7$)

	$\tilde{\nu}$ (cm^{-1})				$\Delta\nu$ (cm^{-1})	assignment
	gas phase ^a	neon matrix ^b	solution ^c	theory ^d		
HC_{14}H	37667	36377	33898	38098	0	0_0^0
	39644				1977	$\nu_{\text{C}\equiv\text{C}}$
	41622				3954	$2\nu_{\text{C}\equiv\text{C}}$
	43485				5818	$3\nu_{\text{C}\equiv\text{C}}$
HC_{12}H	40371	38971	36563	40876	0	0_0^0
	42406				2036	$\nu_{\text{C}\equiv\text{C}}$
	44426				4055	$2\nu_{\text{C}\equiv\text{C}}$
	46350				5979	$3\nu_{\text{C}\equiv\text{C}}$
HC_{10}H	43784		39920	44345	0	0_0^0
	45906				2122	$\nu_{\text{C}\equiv\text{C}}$

^a This work. ^b Reference 15. ^c Reference 14. ^d Reference 18.

single-triple bond length alternation.^{19,20} It can be inferred, on the basis of the spectral analysis of the ${}^1\Sigma_u^+$ excited state that the acetylenic stretching frequency decreases with increasing chain length, suggesting a greater delocalization of the π electron cloud and therefore a less pronounced bond length alternation in the excited state. Theoretical investigation on the ${}^1\Sigma_u^+$ excited-state geometries in the longer chains have not been reported thus far. However, a CASSCF study²⁰ on the smaller members HC_4H , HC_6H , and HC_8H indicates that the bond length equalizes in the middle of the chain and therefore a cumulenic structure for the excited state.

The oscillator strength (f) of the ${}^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$ transition in HC_{2n}H increases with the chain length. For $n = 5, 6$, and 7 the theoretical f value is around $6, 7$, and 8 , respectively.¹⁸ This corresponds to ~ 0.1 ns lifetime of the ${}^1\Sigma_u^+$ state, assuming that the fluorescence quantum yield is unity. However, the width of the observed bands indicates a much shorter lifetime. The width obtained from a Lorentzian fit of the recorded peaks is in the range of $300-500 \text{ cm}^{-1}$. This corresponds to a lifetime in the sub picosecond time scale. Thus internal conversion is the dominant decay pathway of the excited electronic state. The decay characteristics of the excitation-ionization process were measured by varying the pump-probe delay. The exponential decay gave a time constant in the range of $0.2-4 \mu\text{s}$. This long lifetime corresponds to the slowest step in the excitation-ionization scheme. The prepared ${}^1\Sigma_u^+$ excited state undergoes rapid internal conversion to higher vibrational levels of the ${}^1\Sigma_g^+$ ground state or gets trapped in a long-lived excited state, which could be a ${}^3\Sigma_u$ or a ${}^3\Delta_u$ state arising from the same excited-state configuration. The molecule then absorbs a second photon from this intermediate state producing ions which are detected. The microsecond time constants appear to be the lifetime of this latter state.

The gas phase spectrum of longer polyacetylenes, HC_{2n}H ($n = 5-7$) presented here provides the means to identify these molecules remotely by UV spectroscopy in environments such as the atmosphere of Titan. It is generally understood that the formation of polyacetylenes on Titan is initiated by the photodissociation of C_2H_2 creating a C_2H radical that reacts with

another C_2H_2 molecule, producing C_4H_2 . The longer chains also photodissociate, forming C_{2n}H radicals that once again react with acetylene, creating HC_{2n}H chains. In a recent review on polyynes,¹¹ the authors calculated synthetic absorption cross sections using analytical expressions for the origin and the acetylenic stretching frequencies of the ${}^1\Sigma_u^+ \leftarrow X^1\Sigma_g^+$ system in these chains. The absorption cross section was used to derive photolysis rates and predict relative abundances ($\text{HC}_{2n}\text{H}/\text{HC}_2\text{H}$) of longer species. The spectrum presented here provides experimental verification of the UV absorption spectral region in HC_{2n}H ($n = 5-7$). This information can be used to obtain improved absorption cross sections that can be extended to predict the relative abundances of these species with better accuracy.

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