Electronic Absorption Spectra of the Protonated Polyacetylenes $H_2C_nH^+$ ($n = 4, 6, 8$) in Neon Matrixes

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Received: May 1, 2006; In Final Form: June 28, 2006

Electronic absorption spectra of the protonated polyacetylenic chains $H_2C_nH^+$ ($n = 4, 6, 8$) and the neutral H_2C_8H have been observed in 6 K neon matrixes after mass selection. The wavelength of the $H_2C_nH^+$ electronic transitions depends quasi-linearly on n, typical of carbon chains. The origin band is at 286.0, 378.6, and 467.6 nm for $n = 4$, 6, and 8, respectively. Two ground-state vibrations of $H_2C_4H^+$ in the IR absorption spectrum were also detected. On the basis of the spectroscopic trends and the assignment of the vibrational frequencies in the ground and excited electronic states, it is concluded that the $H_2C_nH^+$ species are C_{2v} linear carbon chains with one H atom on one end and two on the other.

Introduction

Unsaturated hydrocarbons with a linear carbon backbone are important constituents of the interstellar medium (ISM).[1] Highly polar carbon chain radicals[2−4] C_nH ($n = 2-8$) and cumulenes[5,6] H_2C_n ($n = 3, 4, 6$) have been detected in dark molecular clouds, and circumstellar shells of carbon reach stars by means of radio astronomy. One can expect that the nonpolar isomers of cumulenes−polyacetylenes ($HC_{2n}H$) should also be abundant in such environments, although they cannot be observed via microwave spectroscopy.

Acetylene and diacetylene were detected a long time ago in hydrocarbon-rich planetary atmospheres in the solar system.[7] Diacetylene is formed from simple hydrocarbons in the upper atmosphere as a result of chemical reactions driven by the solar UV photons. It plays a similar role as ozone on Earth shielding the lower atmospheric layers against UV photons. Larger polyacetylenes were predicted to be present in this environment;[8] however, they have not yet been observed. Recently, diacetylene and triacetylene were detected with the Infrared Space Observatory in the circumstellar medium.[9]

According to current models, most chemical reactions in the ISM are between ions and molecules. Important intermediates in the hydrocarbon reaction network leading to production of linear carbon chain radicals C_nH and cumulenes H_2C_n are polyacetylene cations and protonated polyacetylenes $H_2C_{2n}H^+$.[10] Therefore, the spectroscopic study of these species is also of interest related to astrochemistry. Among them, only the polyacetylene cations have been extensively studied so far in noble gas matrixes[11,12] and the gas phase[13,14] by means of electronic and vibrational spectroscopy. The protonated counterparts are still elusive with the exception of $H_2C_3H^+$, the electronic absorption spectrum of which has been measured in a neon matrix.[15] The next member, $H_2C_4H^+$, of this homologous series has been studied only by mass spectrometry[16−18] and quantum mechanical methods.[18−21] In this paper, the electronic absorption spectra of protonated diacetylene ($H_2C_4H^+$), triacetylene ($H_2C_6H^+$), and tetraacetylene ($H_2C_8H^+$) cations isolated in neon matrixes are reported.

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Experimental Section

The experimental setup has been described.[22] The $C_nH_3^+$ ($n = 4, 6, 8$) cations were produced in an electron impact ion source from diacetylene; $C_4H_3^+$ also from benzene and dimethylacetylene. The precursor molecules were mixed with helium in an 1:3 ratio. The exit aperture of the ion source was reduced in order to increase the inner pressure and enhance production of larger $C_nH_k^+$ ($n > 4$) cations. Experimental conditions (e.g., pressure in the source, temperature of filament, extraction potential) were optimized for the ion of interest. After extraction from the source, ions were guided by means of electrostatic lenses to a 90° bender to get rid of neutral molecules, and then to a quadrupole mass filter. Mass-selected ions with near-unity resolution were co-deposited with neon during 1−2 h onto a rhodium-coated sapphire matrix substrate held at 6 K. The energy of the ions arriving at the surface was ∼50 eV, which led to their partial fragmentation. The newly detected electronic transition of $C_4H_3^+$ has a low oscillator strength, and its absorption bands were weak (low signal-to-noise ratio). Because of this, an electron scavenger (N_2O) was occasionally mixed with neon in concentrations of 1:300 to suppress ion neutralization during deposition. N_2O molecules readily accept electrons, preventing their recombination with cations. Thus, using a scavenger, one can significantly increase the intensity of cationic absorptions. Typical integrated ion currents on the substrate for the $C_4H_3^+$, $C_6H_3^+$, and $C_8H_3^+$ ions were 50, 10, and 8 μC, respectively. Irradiation of the matrix (30 min) with a medium pressure mercury lamp was used to neutralize the trapped cations. UV photons release electrons from weakly bonded anions, which in turn recombine with the cations. Thus, photobleaching helps to distinguish charged and neutral species. Electronic absorption spectra have been measured in the 220−1100 nm spectral range by using a waveguide technique.[23] Infrared spectra have been measured in the 1100−12000 cm^{-1} region by a Fourier transform spectrometer applying a double reflection method.[24]

Observations

$C_4H_3^+$. Mass-selected deposition of $C_4H_3^+$ ($m/z = 51$) revealed two electronic absorption band systems. The first one with origin at 507.4 nm is known and belongs to the

10.1021/jp062657y CCC: $33.50
Published on Web 08/08/2006

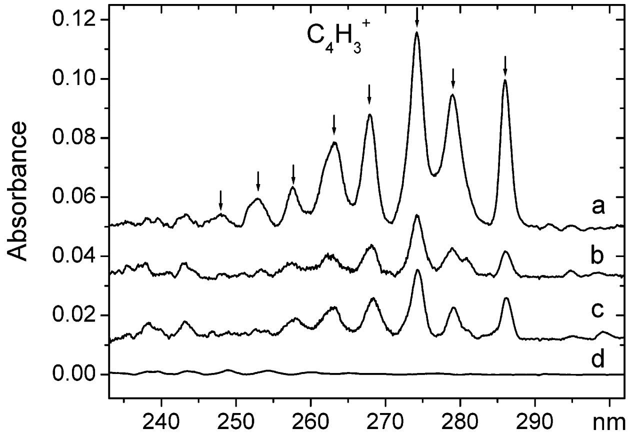

Figure 1. Electronic absorption spectra of the $C_4H_3^+$ cation in 6 K neon matrixes obtained after mass-selected deposition with a mixture of neon and electron scavenger (N_2O) in a proportion of 300:1 (trace a), after UV irradiation of the same matrix (trace b), after $C_4H_3^+$ deposition without electronic scavenger (trace c), and after deposition of $C_4H_2^+$ (trace d).

$A^2\Pi_u \leftarrow X^2\Pi_g$ transition of the HC_4H^+ cation,[25] which is produced by detachment of a hydrogen atom from $C_4H_3^+$ (fragmentation during deposition). A new system with origin at 286.0 nm is also detected (Figure 1). Its absorption pattern was independent of the selected precursor. The intensity of this system decreases after UV irradiation of the matrix (compare traces a and b), which indicates its ionic origin. In the presence of the electron scavenger N_2O (trace a), the intensity of the new bands was stronger than in a pure neon matrix (trace c), although the deposited charges (integral currents) of $C_4H_3^+$ ions were practically the same in both cases. This leads to the conclusion that the carrier of the new absorption is positively charged. Mass-selected deposition of $C_4H_2^+$ ($m/z = 50$) (trace d) did not show a similar pattern; neither did C_4H^+ deposition. Therefore, the new system of bands with the onset at 286.0 nm can be assigned to the $C_4H_3^+$ cation and not to one of its fragments such as $C_4H_2^+$ or smaller. Positions of the origin band and vibronic components of the new transition are given in Table 1. Absorptions of smaller fragments (C_4H, C_4, C_3) of the deposited ion were also detected, but only very weakly. This shows that the fragmentation, except for one H-atom loss, is quite negligible, supporting the proposed assignment.

The infrared vibrational spectrum of $C_4H_3^+$ reveals two new absorptions located at 2086 and 2949 cm^{-1} (Figure 2, Table 1) which are not present in the case of $C_4H_2^+$ deposition and behave in a manner similar to that of the UV bands of $C_4H_3^+$. Hence, they can be assigned to the latter cation. Matrix site effect is responsible for the doublet structure of both peaks. Molecules or ions of interest can occupy different positions in a neon cage having slightly different stabilization energies, which leads to a complex structure of the spectral lines.

$C_6H_3^+$. After $C_6H_3^+$ ($m/z = 75$) deposition, one known and one new electronic absorption were observed. The system with origin band at 604.6 nm is the $A^2\Pi_g \leftarrow X^2\Pi_u$ transition of the HC_6H^+ ion,[11] produced by H-atom loss during the impact on the matrix substrate. The new system with the onset at 378.6 nm together with the absorption band of N_2^+, a common matrix impurity, is seen in Figure 3. UV irradiation of the matrix (compare traces a and b) led nearly to the extinction of the new absorptions indicating their ionic origin. Mass-selected deposition of $C_6H_2^+$ ($m/z = 74$) (traces c and d) did not reveal the same system of bands. Traces c and d were normalized to have the same intensity of the HC_6H^+ $A^2\Pi_g \leftarrow X^2\Pi_u$ absorption system, as in the case of $C_6H_3^+$ deposition (traces a and b). C_6H^+ has recently been studied in a neon matrix, but its absorptions fall in the visible spectral range.[26] Therefore, the new system of bands with origin at 378.6 nm has been assigned to the $C_6H_3^+$ cation. Positions of vibronic components are given in Table 1. Very weak known bands of the smaller fragments (C_6H^+, C_6H, C_3) were also detected.

$C_8H_3^+$ and C_8H_3. Deposition of $C_8H_3^+$ ($m/z = 99$) revealed the known $A^2\Pi_u \leftarrow X^2\Pi_g$ band system of HC_8H^+ with origin

TABLE 1: Observed Electronic and Vibrational Absorption Bands for $C_nH_3^+$ ($n = 4, 6, 8$) and C_8H_3 in 6 K Neon Matrixes

species	λ/nm	$\tilde{\nu}$/cm^{-1}	$\Delta\tilde{\nu}$/cm^{-1}	assignment
$C_4H_3^+$	286.0	34965	0	0_0^0
	279.0	35842	877	CC str
	274.2	36470	1505	CC str
	267.9	37327	2362	1505 + 877
	263.1	38008	3043	CH str
	257.6	38820	3855	2 × 1505 + 877
	253.0	39526	4561	1505 + 3043
	248.0	40323	5358	877 + 1505 + 3043
$C_6H_3^+$	378.6	26413	0	0_0^0
	369.9	27034	621	CC str
	357.3	27988	1575	CC str
	353.0	28329	1916	CC str
	349.7	28596	2183	621 + 1575
	338.7	29525	3112	CH str
	334.6	29886	3473	1575 + 1916
$C_8H_3^+$	467.6	21386	0	0_0^0
	457.5	21858	472	CC str
	442.6	22594	1208	
	436.7	22899	1513	CC str
	433.4	23073	1687	
	427.9	23370	1984	CC str
	419.4	23844	2458	1984 + 472
	410.3	24372	2986	CH str
	402.3	24857	3471	2986 + 472
C_8H_3	358.5	27894	0	0_0^0
	334.4	29904	2010	CC str
	318.4	31407	3513	

IR

	$\tilde{\nu}$/cm^{-1}	assignment
$C_4H_3^+$	2086, 2093	CC str
	2949, 2953	CH str

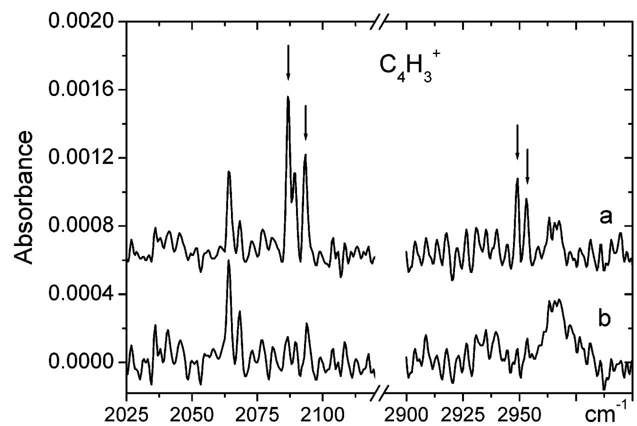

Figure 2. IR absorption spectra of the $C_4H_3^+$ cation in a 6 K neon matrix after mass-selected deposition (trace a) and after UV irradiation of the same matrix (trace b).

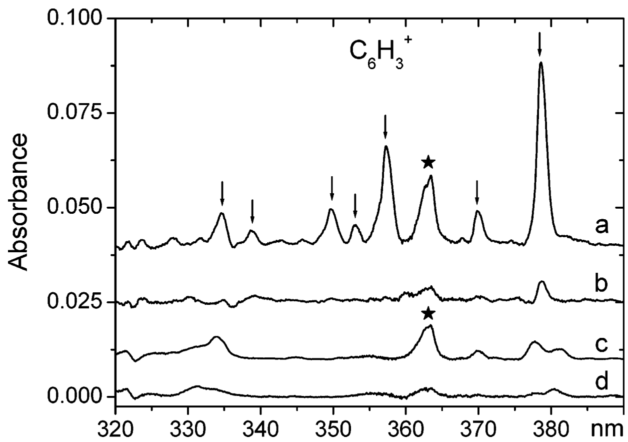

Figure 3. Electronic absorption spectra of the $C_6H_3^+$ cation in a 6 K neon matrix obtained after mass-selected deposition (trace a), after UV irradiation of the same matrix (trace b), after deposition of $C_6H_2^+$ (trace c), and after UV irradiation of that matrix (trace d). Spectra in traces c and d are normalized to have equal intensity of the $C_6H_2^+$ $A^2\Pi_g \leftarrow X^2\Pi_u$ absorption (origin at 604.6 nm, not shown on figure) after $C_6H_3^+$ and $C_6H_2^+$ depositions (traces a and c) and also after irradiation (traces b and d). The bands marked with a star correspond to the absorption of the N_2^+ ion.

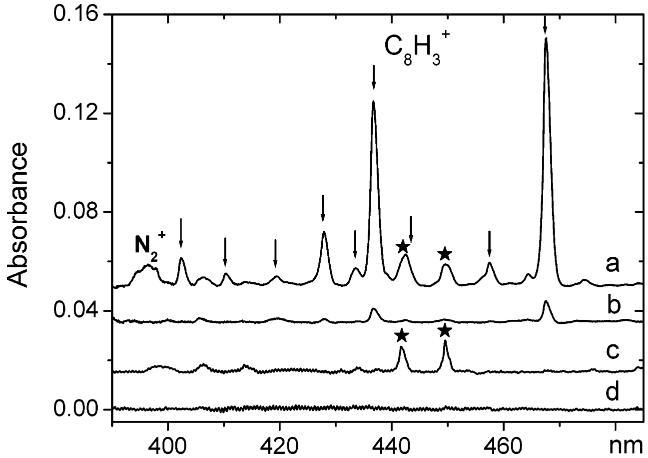

Figure 4. Electronic absorption spectra of the $C_8H_3^+$ cation in a 6 K neon matrix after mass-selected deposition (trace a), after UV irradiation of the same matrix (trace b), after deposition of $C_8H_2^+$ (trace c), and after UV irradiation of that matrix (trace d). Spectra in traces c and d are normalized to have equal intensity of the $C_8H_2^+$ $A^2\Pi_u \leftarrow X^2\Pi_g$ absorption (origin at 713.2 nm, not shown on figure) after $C_8H_3^+$ and $C_8H_2^+$ depositions (traces a and c) and also after irradiation (traces b and d). The bands marked with stars correspond to the absorptions of $C_8H_2^+$.

at 713.2 nm,[11] a result of fragmentation. A new electronic absorption with onset at 467.6 nm was observed (Figure 4 traces a and b). Spectra after deposition of $C_8H_2^+$ (traces c and d) were normalized to have the same intensity as the HC_8H^+ $A^2\Pi_u \leftarrow X^2\Pi_g$ transition, as in the case of $C_8H_3^+$ deposition. Two medium-intensity bands marked with stars can be assigned to other absorptions of HC_8H^+. Their intensity was proportional to that of the HC_8H^+ transition at 713.2 nm, before and after UV irradiation of the matrix, independent of the experiment or exact mass selection. Somewhat better spectral resolution was used to obtain traces c and d. The new system of bands (marked with arrows) with the onset at 467.6 nm (Table 1) disappears after UV irradiation and is not present in the case of $C_8H_2^+$ and C_8H^+ [26] deposition and, hence, can be assigned to the $C_8H_3^+$

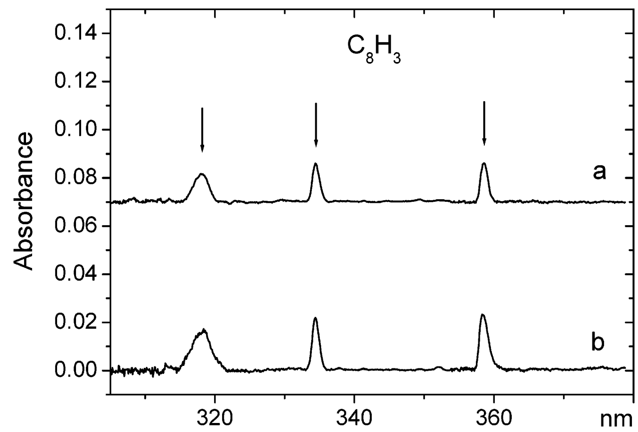

Figure 5. Electronic absorption spectra of the C_8H_3 molecule in a 6 K neon matrix after mass-selected deposition (trace a) and after UV irradiation of the same matrix (trace b).

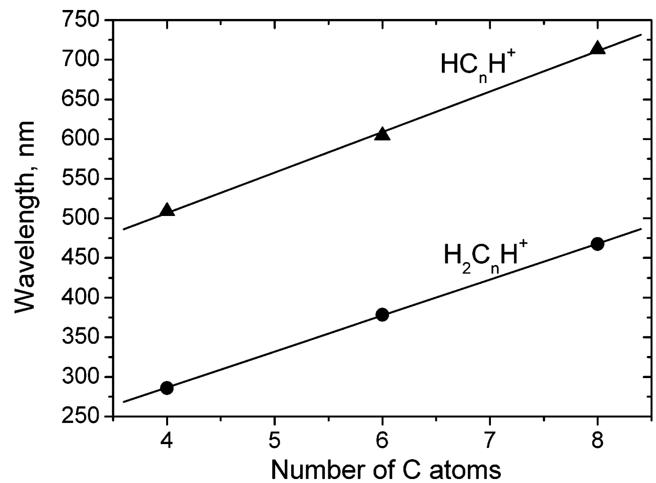

Figure 6. Wavelengths of the origin bands observed for the protonated polyacetylenic chains $H_2C_nH^+$ (circles) and for the known $A^2\Pi \leftarrow X^2\Pi$ transitions of the HC_nH^+ chains[11] (triangles) in neon matrixes versus number of C atoms. Solid lines are linear fits.

cation. The peak at 442.6 nm (trace a) appears to be a superposition of the HC_8H^+ band (trace c) and the $C_8H_3^+$ vibronic component, as can be seen from the relative intensities of the lines marked with a star. Very weak absorptions of C_8H were also detected.

Other new absorptions in the UV spectral range were also observed after $C_8H_3^+$ mass-selected deposition (Figure 5). These bands increase in intensity after UV exposure (compare traces a and b), and thus, they must originate from a neutral molecule. They were not detected after $C_8H_2^+$ or C_8H^+ depositions and are assigned to the absorption of neutral C_8H_3 (Table 1).

Discussion

The wavelengths of the origin bands in the electronic transitions of the $C_nH_3^+$ ($n = 4, 6, 8$) ions are plotted versus n in Figure 6. A near-linear behavior typical for carbon chains is evident.[22] The corresponding data for the HC_nH^+ linear chains[11] ($A^2\Pi \leftarrow X^2\Pi$ transitions) are shown for comparison. The slopes of the linear fits for the $C_nH_3^+$ and HC_nH^+ chains are almost equal, suggesting similar structures. Absorption bands are more intense for larger $C_nH_3^+$ ions despite their smaller concentrations in the matrix. Hence, the oscillator strength of the newly detected $C_nH_3^+$ transitions grows with n, as for other carbon chains.[22]

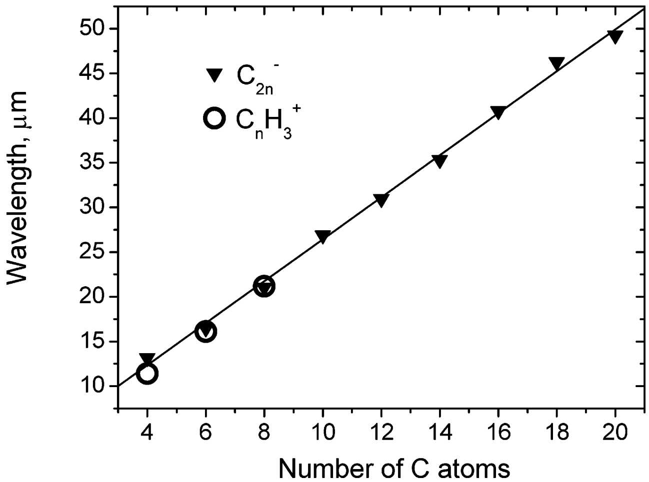

Figure 7. Wavelengths of the lowest-energy totally symmetric vibrations of the C_{2n}^- ($n = 2-10$) carbon chains (filled triangles) and the $H_2C_nH^+$ ($n = 4, 6, 8$) chains (open circles) in neon matrixes versus number of C atoms.

Ground-state geometry optimizations of $C_4H_3^+$ by different ab initio methods have been carried out;[19−21,27,28] the most extensive work took six different structural isomers into consideration.[18] Although there are some contradictions between the reported relative total energies of $C_4H_3^+$ isomers, the linear C_{2v} $H_2C_4H^+$ structure is invariably considered to be the most stable one, with a second-lowest structure lying ~0.7−1.5 eV higher. Thus, the isomer $H_2C_4H^+$ and the longer ones $H_2C_6H^+$ and $H_2C_8H^+$ with C_{2v} symmetry are considered the most plausible structures for the observed electronic absorptions in Figures 1, 3, and 4. Presumably, the structure of C_8H_3 is the same as that of $C_8H_3^+$, because it is formed during neutralization of the cation in the matrix (C_8H_3 absorptions increase after UV irradiation).

Electronic absorption spectra in 6 K neon matrixes reveal only the exited-state vibrational energy levels of the investigated molecule. This is because at 6 K only the zero vibrational level in the ground state is populated. In contrast, IR absorption spectra probe the ground state. The vibrational frequencies inferred from the spectra in the ground and excited states are listed in Table 1.

The C−H stretching vibration in the CH_2 group was detected for all the $C_nH_3^+$ ($n = 4, 6, 8$) ions. The frequencies of this mode in the excited electronic state of the cations are 3043, 3112, and 2986 cm^{-1} for $n = 4$, 6, and 8, respectively. In the IR spectra of $C_4H_3^+$, this vibration is observed at 2949 cm^{-1}. These values are close to the frequencies of this mode at 3026 and 3015 cm^{-1} for the structurally relevant neutral molecules ethylene and allene.[29] The band that corresponds to the stretching of the C−C bonds is also seen in the electronic spectra of $C_nH_3^+$ (i.e., in the excited states) at 1916 and 1984 cm^{-1} for $n = 6$ and 8. The C−C stretch in the ground state of $C_4H_3^+$ is observed at 2086 cm^{-1}. The frequency of this mode was predicted by CEPA-1 calculations at 2010 ± 10 cm^{-1}.[21]

A strong vibronic band in the $C_nH_3^+$ electronic absorption spectra lies 1505, 1575, and 1513 cm^{-1} to higher energy of the origin band for $n = 4$, 6, and 8. Its intensity indicates considerable excited-state geometry change along this mode. Such a vibrational frequency is seldom observed in the electronic spectra of carbon chains. The frequency of this mode is higher than that of the CH_2 scissoring vibration in the ground state of many structurally relevant molecules (e.g., in ethylene, it is at 1342 cm^{-1}; in allene, at 1443 cm^{-1}).[29] Ground-state normal-mode analysis (B3LYP/6-311G* ab initio calculations)[30] shows that the closest totally symmetric vibrations are the CH_2 scissoring at 1321 cm^{-1} and the carbon chain stretch at 1855 cm^{-1}. Excited-state vibrations are usually lower in frequency than in the ground state, and thus, the strong vibronic lines at ~1500 cm^{-1} presumably correspond not to the scissoring mode but to the carbon chain stretching.

The lowest-frequency totally symmetric vibration of a linear carbon skeleton is inversely proportional to the size of a considered molecule. This vibration is detected in the excited state of $C_nH_3^+$ at 877, 621, and 472 cm^{-1} for $n = 4$, 6, and 8 (Table 1). This regularity can be seen if one plots the wavelengths of the C_{2n}^- ($n = 2-10$) carbon chains lowest-energy vibrations[31] versus the number of C atoms (Figure 7). Other carbon chains (e.g., $C_{2n}H$, C_{2n}, $HC_{2n}H^+$)[11,31] behave in the same way. The wavelengths of the $C_nH_3^+$ vibrations (open circles in Figure 7) lie on the same line as the ones of the C_{2n}^- chains.

Therefore, the vibrational frequencies obtained from the $C_nH_3^+$ spectra confirm the presence of the CH_2 group and the linear carbon skeleton supporting the assignment to the protonated polyacetylene structure $H_2C_nH^+$ with C_{2v} symmetry. The observation of the electronic transitions of this class of ions, $C_nH_3^+$, opens the way to gas-phase studies and direct comparisons with astronomical data.

Acknowledgment. This work has been supported by the Swiss National Science Foundation (project 200020-100019).

References and Notes

(1) McCarthy, M. C.; Travers, M. J.; Kovács, A.; Gottlieb, C. A.; Thaddeus, P. *Astrophys. J. Suppl. Ser.* **1997**, *113*, 105.
(2) Cernicharo, J.; Guélin, M. *Astron. Astrophys.* **1996**, *309*, L27.
(3) Guélin, M.; Cernicharo, J.; Travers, M. J.; McCarthy, M. C.; Gottlieb, C. A.; Thaddeus, P.; Ohishi, M.; Saito, S.; Yamamoto, S. *Astron. Astrophys.* **1997**, *317*, L1.
(4) Bell, M. B.; Feldman, P. A.; Watson, K. G.; McCarthy, M. C.; Travers, M. J.; Gottlieb, C. A.; Thaddeus, P. *Astrophys. J.* **1999**, *518*, 740.
(5) Langer, W. D.; Velusamy, T.; Kuiper, T. B. H.; Peng, R.; McCarthy, M. C.; Travers, M. J.; Kovács, A.; Gottlieb, C. A.; Thaddeus, P. *Astrophys. J.* **1997**, *480*, L63.
(6) Kawaguchi, K.; Kaifu, N.; Ohishi, M.; Ishikawa, S.-I.; Hirahara, Y.; Yamamoto, S.; Saito, S.; Takano, S.; Murakami, A.; Vrtilek, J. M.; Gottlieb, C. A.; Thaddeus, P.; Irvine, W. M. *Publ. Astron. Soc. Jpn.* **1991**, *43*, 607.
(7) Kunde, V. G.; Aikin, A. C.; Hanel, R. A.; Jennings, D. E.; Maguire, W. C.; Samuelson, R. E. *Nature (London)* **1981**, *292*, 686.
(8) Shindo, F.; Benilan, Y.; Guillemin, J.-C.; Chaquin, P.; Jolly, A.; Raulin, F. *Planet. Space Sci.* **2003**, *51*, 9.
(9) Cernicharo, J.; Heras, A. M.; Tielens, A. G. G. M.; Pardo, J. R.; Herpin, F.; Guélin, M.; Waters, L. B. F. M. *Astrophys. J.* **2001**, *546*, L123.
(10) Turner, B. E.; Herbst, E.; Terzieva, R. *Astrophys. J. Suppl. Ser.* **2000**, *126*, 427.
(11) Freivogel, P.; Fulara, J.; Lessen, D.; Forney, D.; Maier, J. P. *Chem. Phys.* **1994**, *189*, 335.
(12) Szczepanski, J.; Wang, H.; Jones, B.; Arrington, C. A.; Vala, M. T. *Phys. Chem. Chem. Phys.* **2005**, *7*, 738.
(13) Pfluger, D.; Motylewski, T.; Linnartz, H.; Sinclair, W. E.; Maier, J. P. *Chem. Phys. Lett.* **2000**, *329*, 29.
(14) Pfluger, D.; Sinclair, W. E.; Linnartz, H.; Maier, J. P. *Chem. Phys. Lett.* **1999**, *313*, 171.
(15) Wyss, M.; Riaplov, E.; Maier, J. P. *J. Chem. Phys.* **2001**, *114*, 10355.
(16) Deakyne, C. A.; Meot-Ner, M.; Buckley, T. J.; Metz, R. *J. Chem. Phys.* **2001**, *86*, 2334.
(17) Scott, G. B. I.; Fairley, D. A.; Freeman, C. G.; McEwan, M. J.; Adams, N. G.; Babcock, L. M. *J. Phys. Chem. A* **1997**, *101*, 4973.
(18) Schröder, D.; Loos, J.; Schwarz, H.; Thissen, R.; Roithova, J.; Herman, Z. *Int. J. Mass Spectrom.* **2003**, *230*, 113.
(19) Anand, S.; Schlegel, H. B. *J. Phys. Chem. A* **2005**, *109*, 11551.
(20) Petrie, S.; Knight, J. S.; Freeman, C. G.; Maclagan, R. G. A. R.; McEwan, M. J.; Sudkeaw, P. *Int. J. Mass Spectrom. Ion Processes* **1991**, *105*, 43.

(21) Botschwina, P.; Schramm, H.; Sebald, P. *Chem. Phys. Lett.* **1990**, *169*, 121.
(22) Maier, J. P. *Chem. Soc. Rev.* **1997**, *26*, 21.
(23) Bondybey, V. E.; Sears, T. J.; English, J. H.; Miller, T. A. *J. Chem. Phys.* **1980**, *73*, 2063.
(24) Batalov, A.; Fulara, J.; Shnitko, I.; Maier, J. P. *Chem. Phys. Lett.* **2005**, *404*, 315.
(25) Bondybey, V. E.; English, J. H. *J. Chem. Phys.* **1979**, *71*, 777.
(26) Shnitko, I.; Fulara, J.; Batalov, A.; Gillery, C.; Masso, H.; Rosmus, P.; Maier, J. P. *J. Phys. Chem. A* **2006**, *110*, 2885.
(27) Hori, K.; Yamabe, T.; Tachibana, A.; Asai, Y.; Fukui, K.; Kobayashi, S.; Taniguchi, H. *THEOCHEM* **1987**, *153*, 295.
(28) Milburn, R. K.; Bohme, D. K.; Hopkinson, A. C. *Int. J. Mass Spectrom.* **2000**, *195*/*196*, 393.
(29) Shimanouchi, T. *Tables of Molecular Vibrational Frequencies Consolidated*; National Bureau of Standards; U.S. Government Printing Office: Washington, DC, 1972; Vol. 1, p 1.
(30) Dr. P. Kolek, private communication.
(31) Freivogel, P.; Fulara, J.; Jakobi, M.; Forney, D.; Maier, J. P. *J. Chem. Phys.* **1995**, *103*, 54.