Electronic Absorption Spectra of the Protonated Polyacetylenes H$_2$C$_n$H$^+$ ($n = 4, 6, 8$) in Neon Matrixes

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Electronic absorption spectra of the protonated polyacetylenic chains H$_2$C$_n$H$^+$ ($n = 4, 6, 8$) and the neutral H$_2$C$_n$H have been observed in 6 K neon matrixes after mass selection. The wavelength of the H$_2$C$_n$H$^+$ 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$_2$C$_n$H$^+$ 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$_2$C$_n$H$^+$ species are C$_{2n}$ 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). Highly polar carbon chain radicals$^{2-4}$ C$_n$H ($n = 2-8$) and cumulenes$^{5,6}$ H$_2$C$_{2n}$ ($n = 3, 4, 6$) 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 UV photons. It plays a similar role as ozone on Earth shielding

Experimental Section

The experimental setup has been described.$^{22}$ The C$_n$H$_{3+}$ ($n = 4, 6, 8$) cations were produced in an electron impact ion source from diacetylene; C$_4$H$_3^+$ 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$_n$H$_{3+}$ ($n > 4$) 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 $\sim$50 eV, which led to their partial fragmentation. The newly detected electronic transition of C$_4$H$_3^+$ has a low oscillator strength, and its absorption bands were weak (low signal-to-noise ratio). Because of this, an electron scavenger (N$_2$O) was occasionally mixed with neon in concentrations of 1:300 to suppress ion neutralization during deposition. N$_2$O 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$_4$H$_3^+$, C$_6$H$_5^+$, and C$_8$H$_5^+$ ions were 50, 10, and 8 $\mu$C, 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$_4$H$_3^+$. Mass-selected deposition of C$_4$H$_3^+$ ($m/z = 51$) revealed two electronic absorption band systems. The first one with origin at 507.4 nm is known and belongs to the
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A^2Πg ← X^2Πg transition of the HC₆H⁺ cation,25 which is produced by detachment of a hydrogen atom from C₄H₃⁺ (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 N₂O (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 C₄H₃⁺ 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 C₆H₃⁺ (m/z = 50) (trace d) did not show a similar pattern; neither did C₄H⁺ deposition. Therefore, the new system of bands with the onset at 286.0 nm can be assigned to the C₄H₃⁺ cation and not to one of its fragments such as C₅H₂⁺ or smaller. Positions of the origin band and vibronic components of the new transition are given in Table 1. Absorptions of smaller fragments (C₄H, C₆, C₃) 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 C₄H₃⁺ reveals two new absorptions located at 2086 and 2949 cm⁻¹ (Figure 2, Table 1) which are not present in the case of C₆H₃⁺ deposition and behave in a manner similar to that of the UV bands of C₄H₃⁺. 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.

C₄H₃⁺. After C₄H₃⁺ (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^2Πg ← X^2Πg transition of the HC₆H⁺ 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 N₂⁺, 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 C₄H₃⁺ (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 HC₆H⁺ A^2Πg ← X^2Πg absorption system, as in the case of C₄H₃⁺ deposition (traces a and b). C₄H⁺ 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 C₄H⁺ cation. Positions of vibronic components are given in Table 1. Very weak known bands of the smaller fragments (C₄H⁺, C₆H, C₃) were also detected.

C₆H₃⁺ and C₄H₃⁺. Deposition of C₆H₃⁺ (m/z = 99) revealed the known A^2Πu ← X^2Πg band system of HC₆H⁺ with origin
at 713.2 nm, 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 \(\text{C}_8\text{H}_2^+\) (trace c) and after UV irradiation of that matrix (trace d) are normalized to have equal intensity of the \(\text{C}_8\text{H}_2^+ A^2\Pi_u \leftarrow X^2\Pi_g\) absorption (origin at 604.6 nm, not shown on figure) after \(\text{C}_8\text{H}_3^+\) and \(\text{C}_8\text{H}_2^+\) depositions (traces a and c) and also after irradiation (traces b and d). The bands marked with stars correspond to the absorption of the \(\text{N}_2^+\) ion.

![Figure 3](image_url)

**Figure 3.** Electronic absorption spectra of the \(\text{C}_6\text{H}_3^+\) 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 \(\text{C}_6\text{H}_2^+\) (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 \(\text{C}_6\text{H}_2^+ A^2\Pi_u \leftarrow X^2\Pi_g\) absorption (origin at 604.6 nm, not shown on figure) after \(\text{C}_6\text{H}_3^+\) and \(\text{C}_6\text{H}_2^+\) depositions (traces a and c) and also after irradiation (traces b and d). The bands marked with stars correspond to the absorptions of \(\text{C}_6\text{H}_2^+\).

![Figure 4](image_url)

**Figure 4.** Electronic absorption spectra of the \(\text{C}_8\text{H}_3^+\) 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 \(\text{C}_8\text{H}_2^+\) (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 \(\text{C}_8\text{H}_2^+ A^2\Pi_u \leftarrow X^2\Pi_g\) absorption (origin at 713.2 nm, not shown on figure) after \(\text{C}_8\text{H}_3^+\) and \(\text{C}_8\text{H}_2^+\) depositions (traces a and c) and also after irradiation (traces b and d). The bands marked with stars correspond to the absorptions of \(\text{C}_8\text{H}_2^+\).

![Figure 5](image_url)

**Figure 5.** Electronic absorption spectra of the \(\text{C}_8\text{H}_3^+\) 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 \(\text{C}_8\text{H}_2^+\) (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 \(\text{C}_8\text{H}_2^+ A^2\Pi_u \leftarrow X^2\Pi_g\) absorption (origin at 713.2 nm, not shown on figure) after \(\text{C}_8\text{H}_3^+\) and \(\text{C}_8\text{H}_2^+\) depositions (traces a and c) and also after irradiation (traces b and d). The bands marked with stars correspond to the absorptions of \(\text{C}_8\text{H}_2^+\).

![Figure 6](image_url)

**Figure 6.** Wavelengths of the origin bands observed for the protonated polyacetylenic chains \(\text{H}_2\text{C}_n\text{H}_n^+\) (circles) and for the known \(A^2\Pi \leftarrow X^2\Pi\) transitions of the \(\text{HC}_n\text{H}_n^+\) chains\(^\text{11}\) (triangles) in neon matrixes versus number of C atoms. Solid lines are linear fits.
higher. Thus, the isomer $H_2C_4H^+$.

The vibrations of the C$_2$H$_n$+ isomers, the linear C$_2$H structure is invariably considered to be the most stable one, with a second-lowest structure lying $\sim$0.7–1.5 eV higher. Thus, the isomer H$_2$CCH$^+$ and the longer ones H$_2$C$_n$H$^+$ and H$_2$C$_n$H$^+$ with $C_{3v}$ symmetry are considered the most plausible structures for the observed electronic absorptions in Figures 1, 3, and 4. Presumably, the structure of C$_4$H$_3$ is the same as that of C$_n$H$_n$+, because it is formed during neutralization of the cation in the matrix (C$_n$H$_n$+ absorptions increase after UV irradiation).

Electronic absorption spectra in 6 K neon matrices reveal only the excited-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$_4$H$_n$+ ($n = 4, 6, 8$) ions. The frequencies of this mode in the excited-state 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$_4$H$_n$+, 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. The band that corresponds to the stretching of the C–C bonds is also seen in the electronic spectra of C$_4$H$_n$+ (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$_4$H$_n$+ is observed at 2086 cm$^{-1}$. The frequency of this mode was predicted by CEPA-1 calculations at 2010 $\pm$ 10 cm$^{-1}$.

A strong vibrionic band in the C$_n$H$_n$+ 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 C$_2$H 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$^{-1}$). Ground-state normal-mode analysis (B3LYP/6-311G* ab initio calculations) 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 $\sim$1500 cm$^{-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$_2$H$_n$+ 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$_2$H$_n$+ ($n = 2–10$) carbon chains lowest-energy vibrations versus the number of C atoms (Figure 7). Other carbon chains (e.g., C$_2$H, C$_3$H, C$_n$H$_2$H$_n$+) behave in the same way. The wavelengths of the C$_2$H$_n$+ vibrations (open circles in Figure 7) lie on the same line as the ones of the C$_2$H$_n$+ chains.

Therefore, the vibrational frequencies obtained from the C$_2$H$_n$+ spectra confirm the presence of the CH$_2$ group and the linear carbon skeleton supporting the assignment to the protonated polyacetylene structure H$_2$C$_n$H$^+$ with $C_{3v}$ symmetry. The observation of the electronic transitions of this class of ions, C$_n$H$_n$+, opens the way to gas-phase studies and direct comparisons with astronomical data.

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References and Notes


(30) Dr. P. Kolek, private communication.