Electronic Gas-Phase Spectrum of the Pentaacetylene Cation[†]

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The origin band of the $A^2\Pi_u-X^2\Pi_g$ electronic transition of the linear pentaacetelyne cation, $HC_{10}H^+$, and isotopic derivatives, $HC_{10}D^+$ and $DC_{10}D^+$, has been recorded in the gas phase. The absorption spectrum was observed by cavity ring down spectroscopy through a supersonic planar plasma expansion. The spectrum comprises both spin−orbit components with resolved P- and R-branches. Contour fits allow the determination of ground and excited state spectroscopic constants.

Introduction

The polyacetylene cations, HC_nH^+, are open-shell species with a $^2\Pi$ ground state. The strong electronic transitions have $^2\Pi_u-X^2\Pi_g$ symmetry and shift to the red with increasing number of carbon atoms. Rotationally resolved electronic spectra have been recorded previously in the gas phase for the even members with $n = 2$ at 255.7 nm,[1] $n = 4$ at 507.0 nm,[2,3] $n = 6$ at 600.4 nm,[4,5] and $n = 8$ at 707.1 nm.[6] Little is known on the next member in the series, the pentaacetylene cation $HC_{10}H^+$. Density functional theory calculations[7] and ion chromatography[8] predict a linear structure. It was shown that $HC_{10}H^+$ is formed in an ion trap upon collision activated processes on polycyclic aromatic hydrocarbons.[9] Furthermore, this cation may be of interest from an astrophysical point of view. It has been argued that electronic transitions of carbon chains may be among the carriers of unidentified absorption features in diffuse interstellar clouds.[10] Particularly longer chains are of interest as these are expected to be photo stable.

The first experimental observation of the $A^2\Pi_u-X^2\Pi_g$ electronic spectrum of $HC_{10}H^+$ was in a neon matrix using mass selective deposition;[11] the transition was found to comprise a strong origin band around 823.3 nm and a series of weaker bands corresponding to vibrational excitation in the upper electronic state. In the case of the smaller polyacetylene cations, the transitions in the gas phase are typically blue-shifted 100−130 cm^{-1} with respect to the matrix value, that is, the unperturbed origin band of $HC_{10}H^+$ is expected between 814.5 and 816.5 nm.

Experiment

The wavelength range around 815.5 nm was scanned using cavity ring down (CRD) spectroscopy. CRD has become a powerful tool for the study of the structural and dynamical properties of molecules in the gas phase.[12] One of the reasons for this success is the conceptual simplicity of a CRD experiment. A small fraction of laser light is coupled into an optical cavity of length L consisting of two mirrors with a reflectivity close to unity. The light leaking out of the cavity has an envelope, which is simply a first-order exponential decay, $\exp(-t/\tau)$. The ring down time, τ, reflects the rate of absorption rather than its magnitude, and as such the method is independent of power fluctuations. In addition, very long absorption path lengths are obtained by confining light tens of microseconds to the cavity. A spectrum is recorded by measuring τ as function of the laser frequency.

In the present experiment, a standard pulsed CRD spectrometer with a resolution of 0.15 cm^{-1} is used to sample a pulsed supersonic plasma, generated by discharging a mixture of 0.3% HCCH (or DCCD or both) in He (−600 V, 100 mA) in the throat of a 300 mm × 300 μm multichannel slit nozzle geometry.[13] This system combines high molecular densities and relatively large absorption path lengths with an effective adiabatic cooling. The best S/N ratios are found when the CRD beam intersects the expansion 3 mm downstream from the nozzle orifice. The light exiting the optical cavity is focused via a narrow band-pass filter onto a broad band Si photodiode and is monitored by a fast oscilloscope. Typical ring down times amount to $\tau = 50$ μs. For a cavity of length $L = 52$ cm, this is equivalent to approximately 29 000 passes through the plasma or an effective absorption path length of 865 m. The present data set is calibrated via the internal reference system of the dye laser, yielding an absolute accuracy on the order of 0.5 cm^{-1} around 815 nm.

Results and Discussion

For an $A^2\Pi_u-X^2\Pi_g$ electronic transition of a linear molecule, one expects to observe two separate bands (each consisting of a P-, Q-, and R-branch) of the two spin−orbit transitions $A^2\Pi_{3/2}-X^2\Pi_{3/2}$ and $A^2\Pi_{1/2}-X^2\Pi_{1/2}$. The intensity ratio of the two bands is determined by the spin−orbit temperature (T_{so}) and the spin−orbit splitting in the ground state (A''). The latter is expected to be close to the value found for the tri- and tetraacetylene cations, −31 cm^{-1}. The minus sign indicates that the ground state is inverted—as was observed for the smaller polyacetylene chains[5,6]—i.e., the $\Omega = 3/2$ component is below $\Omega = 1/2$. The separation between the two bands in the spectrum is given by the difference in spin−orbit constants in excited and ground state ($\Delta A = A' - A''$) and is expected to be on the order of 3 cm^{-1}.

The origin band in the $A^2\Pi_u-X^2\Pi_g$ electronic transition of $HC_{10}H^+$ is shown in the left part of Figure 1. The band contour

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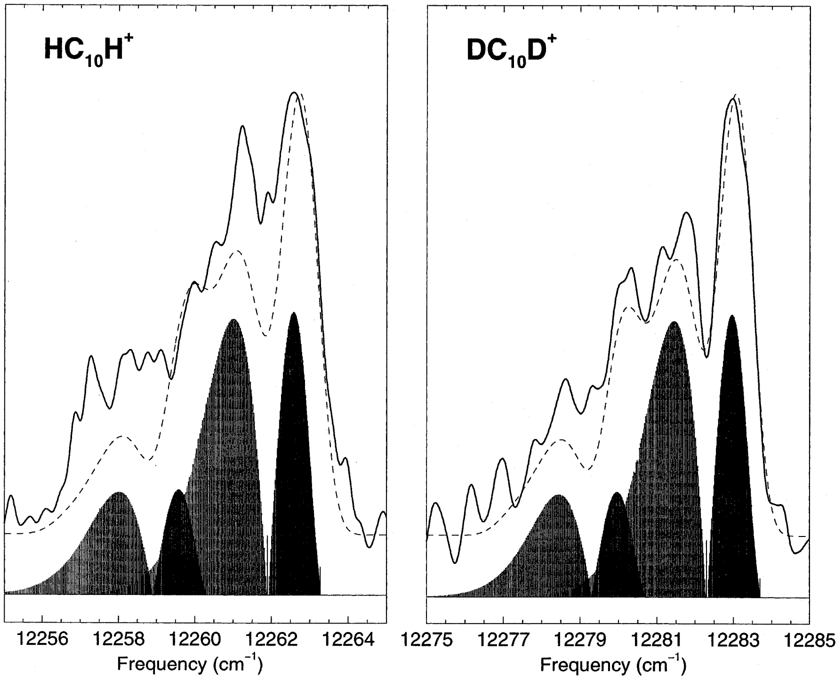

Figure 1. A smoothed laboratory spectrum of the $A^2\Pi_u-X^2\Pi_g$ electronic origin band transition of $HC_{10}H^+$ (left side) and $DC_{10}D^+$ (right side) recorded in absorption using cavity ring down spectroscopy with 0.15 cm^{-1} resolution. Both spin−orbit components are visible, as can be concluded from the stick diagram. The latter shows the simulation for a rotational temperature of $T_{rot} = 45$ K and molecular parameters as listed in Table 1. The dashed line shows the simulation for the unresolved spectrum.

of both spin−orbit components is visible, even though there is some overlap with the absorption lines of another species, presumably C_2. The band is not rotationally resolved because the rotational constant of $HC_{10}H^+$ is on the order of 0.01 cm^{-1} and the best laser resolution obtained with an internal etalon was 0.035 cm^{-1}. In addition, lifetime broadening might occur as result of intramolecular processes. It is possible, however, to interpret the band contours in terms of unresolved P-, Q- and R-branch contours of the $A^2\Pi_{3/2}-X^2\Pi_{3/2}$ and $A^2\Pi_{1/2}-X^2\Pi_{1/2}$ electronic transitions. This is demonstrated in the figure with stick diagrams.

The observed rotational profiles were simulated to determine the band origin position and to estimate the spectroscopic constants, using PGopher.[14] The ground state spin−orbit splitting is assumed to be similar to that found for the tri- and tetraacetylene cations, −31 cm^{-1}. The intensity ratio of the two spin−orbit bands yields $T_{so} = 45(5)$ K, which will be close to the rotational temperature, T_{rot}. This value is higher than that in previous experiments (e.g., ref 15) and a direct consequence of measuring closer to the slit nozzle orifice; further downstream the shoulder at lower energy disappears and only the $A^2\Pi_{3/2}-X^2\Pi_{3/2}$ band is observed. The ground-state rotational constant $B'' = 0.009\,88$ cm^{-1} is calculated from a recent ab initio density functional theory geometry optimization that gives H−C1 = 1.068 Å, C1−C2 = 1.219 Å, C2−C3 = 1.330 Å, C3−C4 = 1.240 Å, C4−C5 = 1.311 Å, and C5−C6 = 1.246 Å,[7] reflecting a single−triple bond alternation.[16] A good simulation is obtained for an origin band value of $T_0 = 12\,260.4(5)$ cm^{-1}, blue-shifted 117 cm^{-1} with respect to the matrix value and with excited-state values $A' = -28$ cm^{-1} (i.e., $\Delta A = 3$ cm^{-1}) and $B' = 0.009\,82$ cm^{-1}. The latter value is expected to be accurate to within a few percent. The ratio $B''/B' = 1.007$ is close to unity; for a chain as long as $HC_{10}H^+$, only a minor change in molecular geometry is expected upon electronic excitation. For smaller chains, the effect is more pronounced. This can be seen from Table 1 in which the parameters of a number of polyacetylene cations HC_nH^+ are compared.

TABLE 1: Comparison of the Spectroscopic Constants of Linear Chains HC_nH^+, DC_nD^+, and HC_nD^{+a}

HC_nH^+

	$n = 4^b$	$n = 6^c$	$n = 8^d$	$n = 10^{e,f}$
T_0	19 722.610(2)	16 654.6873(3)	14 143.1815(5)	12 260.4(5)
B''	0.146 888(22)	0.044 594(3)	0.019 078(9)	0.009 88(3)
B'	0.140 083(22)	0.043 792(3)	0.018 867(9)	0.009 82(3)
B''/B'	1.049	1.018	1.011	1.007
A''	−33.5(1.9)	−31.40(28)	(−31)	(−31)
A'	−31.1(2.0)	−28.41(28)	(−28)	(−28)
ΔA			3	3

HC_nD^+

	$n = 4^g$	$n = 6^c$	$n = 8^g$	$n = 10^f$
T_0	19 731.725(2)	16 670.6168(3)	14 156.3(3)	12 270.6(5)
B''	0.136 599(30)	0.042 573(8)		
B'	0.130 469(30)	0.041 815(8)		
B''/B'	1.047	1.018		
A''	(−33.3)	−32.37(56)		
A'	(−31.1)	−29.42(56)		
ΔA	2.2			

DC_nD^+

	$n = 4^b$	$n = 6^c$	$n = 8^d$	$n = 10^f$
T_0	19 740.683(2)	16 686.5100(3)	14 169.5243(3)	12 280.8(5)
B''	0.127 403(24)	0.040 701(9)	0.017 648(6)	0.009 23(5)
B'	0.121 831(25)	0.039 980(9)	0.017 452(6)	0.009 17(5)
B''/B'	1.046	1.018	1.011	1.007
A''	−33.3(2.0)	−31.31(49)	(−31)	(−31)
A'	−31.1(2.0)	−28.40(49)	(−28)	(−28)
ΔA			3	3

[a] All values are in cm^{-1}. [b] Reference 2. [c] Reference 3. [d] Reference 4. [e] Reference 6. [f] This work. [g] Reference 19.

For larger n, the rotational constants B decrease, the ratio B''/B' decreases as well, and there is a monotonic shift of the origin band to the red. The oscillator strength increases with n, which holds promise for the extension of the experimental approach to measure the electronic spectrum of even longer species.

A confirmation of the assignment of the observed 815.5 nm band to the pentaacetylene cation is provided by the detection of this transition in the partially ($HC_{10}D^+$) and fully deuterated ($DC_{10}D^+$) species. The latter is shown in the right part of Figure 1, approximately 20 cm^{-1} blue-shifted with respect to the $HC_{10}H^+$ band. A good simulation of the observed spectrum is obtained for $B'' = 0.009\ 23(5)\ cm^{-1}$, $B' = 0.009\ 17(5)\ cm^{-1}$, and $T_0 = 12\ 280.8(5)\ cm^{-1}$ (Figure 1). The corresponding stick diagram is shown as well. The spectrum of the monodeuterated chain, $HC_{10}D^+$, has been observed at 12 270.6(5) cm^{-1} but is rather weak, and a contour simulation is not possible. Table 1 summarizes the determined spectroscopic constants for chains HC_nD^+ and DC_nD^+, with $n = 4$, 6, 8, and 10.

This work presents the electronic spectrum of the largest polyacetylene cation measured in the gas phase so far. Nevertheless, a comparison with the hitherto reported diffuse interstellar bands in the near infrared[17,18] shows that there is no absorption apparent at the position of the origin band in the electronic spectrum of $HC_{10}H^+$.

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