The $A\,^3\Sigma^- - X\,^3\Sigma^-$ electronic transition of HC_6N

Olga Vaizert, Tomasz Motylewski, Muriel Wyss, Evgueni Riaplov, Harold Linnartz,[a)]and John P. Maier
Institute for Physical Chemistry, Klingelbergstrasse 80, CH-4056 Basel, Switzerland

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A combined matrix and gas phase study is presented to identify the $A\,^3\Sigma^- - X\,^3\Sigma^-$ electronic transition of the linear triplet isomer of HC_6N and isotopic derivative DC_6N. Absorption spectra have been observed in a 6 K neon matrix after mass selective deposition and in the gas phase by cavity ring down spectroscopy through a supersonic planar plasma. The band origin of the 0_0^0 $A\,^3\Sigma^- - X\,^3\Sigma^-$ electronic transition of HC_6N is determined to be at 21 208.60(5) cm^{-1}, shifted ~30 cm^{-1} to the blue of the neon matrix value. Rotational analysis indicates that the chain is slightly stretched on electronic excitation, yielding $B_0' = 0.027\,92(5)\ cm^{-1}$. Transitions to vibrationally excited levels in the upper $A\,^3\Sigma^-$ state are observed as well. The results are compared with a rotationally resolved spectrum of the 0_0^0 $A\,^3\Sigma_u^- - X\,^3\Sigma_g^-$ electronic transition of the isoelectronic HC_7H species. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1361254]

I. INTRODUCTION

A number of unsaturated linear carbon chains has been discovered in the interstellar gas[1] with the aid of laboratory Fourier transform microwave (FTMW) spectroscopy.[2] The identification of species such as C_nH,[3–5] C_nN,[6] $HC_{2n+1}N$[7] and H_2C_n[8] in the dense interstellar medium, or C_n in circumstellar shells,[9] has strengthened the idea that their electronic transitions are of interest for comparison with diffuse interstellar band features.[10] The latter are observed as absorptions of star-light passing through the diffuse interstellar medium. The systematic laboratory search for the electronic transitions of such chains in the gas phase has become possible following the observation of absorption spectra of mass selected species deposited in a 6 K neon matrix.[11] Recent articles report gas phase electronic spectra of both highly unsaturated[12,13] and pure carbon[14,15] chains, as well as their cations[16] and anions[17,18] and allow for the first time a systematic comparison between laboratory data and astronomical observations.[19–21]

Of particular interest are chains of the form $HC_{2n}N$. Cyanomethylene, HCCN, has been identified both in the laboratory[22,23] and in the interstellar medium.[24] Recently, a cyclic (ring chain) and the linear triplet isomer of both HC_4N[25,26] and HC_6N[26,27] were detected using FTMW spectroscopy. *Ab initio* calculations predict a cyclic singlet ground state structure with a C_3 ring for HC_4N.[28] In the case of HC_6N (and the isoelectronic HC_7H) initially a cyclic singlet structure was calculated,[29] but recent work favours the linear triplet structure as the more stable isomer.[28] This is in agreement with the microwave work on the triplet HC_6N[27] that suggests that the abundance of molecules with a linear geometry is about a factor 10 larger than that with a cyclic structure.

The spectroscopic characteristics of chains of the form HC_nN are desirable not only because of their astrophysical and theoretical importance but also for the identification of such species in plasma and combustion reactions. In this contribution the identification of the $A\,^3\Sigma^- - X\,^3\Sigma^-$ electronic spectrum of the linear triplet chain HC_6N and its isotopic derivative DC_6N is presented. The mass selected species are first codeposited with neon to form a matrix at 6 K. This method has been successfully applied to observe the electronic spectra of homologous series of carbon chains.[11] These data are then used to search for the gas phase transitions. In the present experiment cavity ring down (CRD) spectroscopy through a supersonic planar plasma is applied.

II. EXPERIMENT

A. Neon matrix

The apparatus combines mass selection and matrix isolation spectroscopy.[30] Two different electron impact sources were used to produce either anionic or cationic HC_6N. HC_6N^- anions were produced from a mixture of 33% HC_3N in argon and HC_6N^+ cations from 50% HC_3N in helium. A mixture of 25% C_2D_2 and 25% C_2N_2 in helium was used as precursor for the deuterated species. A 90° deflector and a quadrupole mass spectrometer steered the ion beam onto the matrix, where the mass selected ions were codeposited with excess of neon on a 6 K rhodium coated sapphire plate. Ion currents of 2.3 nA for HC_6N^- and 3.5 nA for HC_6N^+ were obtained. Subsequent neutralisation of the trapped species was achieved by irradiation of the matrix with a medium pressure mercury lamp (λ>230 nm). The absorption spectra were recorded by guiding monochromatized light of a halogen lamp (~0.1 nm bandpass) into the matrix where it was propagated through the thin side in a wave-guide manner[31] onto a photomultiplier. Absorptions were mainly due to mass selected species, but some impurities can arise because of fragmentation.

[a)]Author to whom correspondence should be addressed. Electronic mail: Henricus.Linnartz@unibas.ch

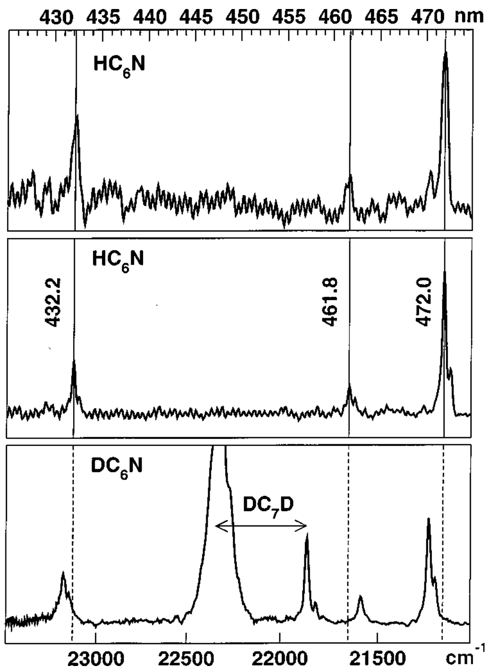

FIG. 1. The $A\,^3\Sigma^- - X\,^3\Sigma^-$ electronic absorption spectrum of HC_6N measured in a 6 K matrix after codeposition of mass selected anions (upper trace) or cations (middle trace) with excess of neon. The lower trace shows the DC_6N spectrum. The shifts upon isotopic substitution are visible.

B. Cavity ring down spectroscopy

The experimental method has been described.[32] A supersonic planar plasma was generated by a discharge through a gas pulse (−500 V, 30 Hz repetition rate) of a 0.25% diacetylene (or dideutero–diacetylene) and 0.25% cyanogen mixture in neon with a backing pressure of 10 bar in the throat of a 3 cm×100 μm multilayer slit nozzle geometry. The CRD beam intersected the plasma expansion ~1 cm downstream. Typically 45 ring down events were averaged at each wavelength. The laser bandwidth was ~0.035 cm^{-1} with an étalon in the dye laser cavity. This is close to the spacing of adjacent rotational transitions and, therefore, care was taken to reduce residual Doppler broadening in the slit expansion below the laser bandwidth by exchanging the primary slotted ceramic plate (see Ref. 32) with a multichannel device. The spectra were calibrated using an external wave meter with an absolute accuracy of 0.01 cm^{-1}.

III. RESULTS AND DISCUSSION

A. Neon matrix spectra

The observed $A\,^3\Sigma^- - X\,^3\Sigma^-$ electronic absorption spectrum of HC_6N in a neon matrix at 6 K shows features characteristic for carbon chains upon excitation of π-electrons; a strong origin band (0_0^0) and several transitions to vibrationally excited levels in the upper electronic state. The upper two traces of Fig. 1 show the matrix absorption spectrum obtained in the anionic and cationic source. The spectrum is dominated by three bands, located at 472.0(2), 461.8(2), and 432.2(2) nm. The band at lowest energy is assigned to the $A\,^3\Sigma^- - X\,^3\Sigma^-$ electronic origin band transition. The weaker band (~467 cm^{-1} to higher energy) involves excitation of a bending mode in the excited state. This is confirmed upon deuterium substitution (lower trace Fig. 1); whereas the two stronger bands shift to higher energy a redshift is found for the band at 462 nm. Similar behavior was observed previously for the bending modes of HC_7H.[33] The two additional bands that appear in the deuterated spectrum are due to DC_7D for which mass discrimination is not effective. The band at highest energy (~432 nm) is separated from the origin by 1950 cm^{-1}, a typical value for a vibrational mode involving excitation of a carbon triple bond ($\nu_{C\equiv C}$). Upon deuterium substitution this value is hardly affected. Table I

TABLE I. Observed bands in the $A\,^3\Sigma^- - X\,^3\Sigma^-$ electronic transition of HC_6N and DC_6N measured in a 6 K neon matrix and in the gas phase.

	Neon matrix				Gas phase	
	λ [nm]	ν [cm^{-1}]	$\Delta\nu$ [cm^{-1}]	I^a	ν [cm^{-1}]	$\Delta\nu$ [cm^{-1}]
HC_6N						
0_0^0	472.0(2)	21 181(10)	0	1.00	21 208.60(5)	0
ν_{bend}	461.8(2)	21 648(10)	467	0.3	⋯	⋯
$\nu_{C\equiv C}$	432.2(2)	23 131(10)	1950	0.5	23 151.2(2)	1942.5
DC_6N						
0_0^0	470.7(2)	21 239(10)	0	1.00	21 282.10(5)	0
ν_{bend}	463.2(2)	21 583(10)	344	0.3	⋯	⋯
$\nu_{C\equiv C}$	431.4(2)	23 174(10)	1935	0.5	23 208.1(2)	1926.0

[a]Relative intensity normalized on the origin band (error ~20%). For HC_6N the average value of the signal obtained in the cationic and anionic source is given.

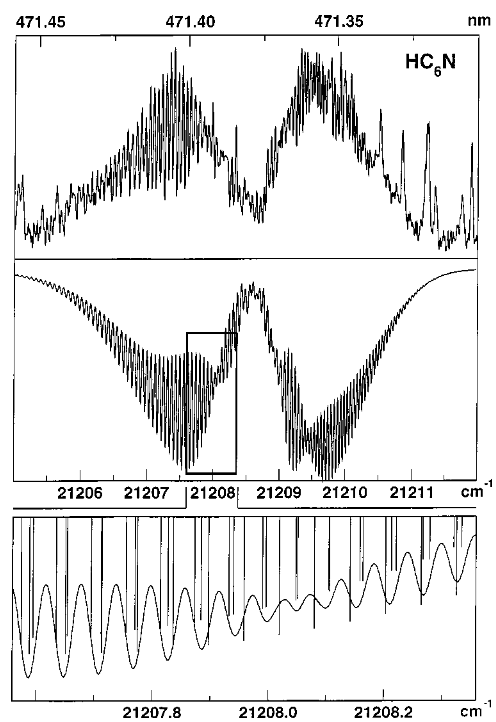

FIG. 2. The $A\,^3\Sigma^- - X\,^3\Sigma^-$ electronic origin band spectrum of HC_6N in the gas phase measured by cavity ring down spectroscopy through a supersonic planar plasma (upper trace) and a simulation (middle trace). The lower part shows the stick diagram for the frequency range defined by the box in the middle trace, demonstrating spectral fading when rotational lines and triplet splittings do not coincide.

lists the wave numbers of all the observed HC_6N and DC_6N bands.

B. Gas-phase spectra

The upper trace of Fig. 2 shows the $A\,^3\Sigma^- - X\,^3\Sigma^-$ electronic origin band transition of HC_6N measured by CRD through the expanding plasma. The spectrum is recorded at rotational resolution and has the spectral features characteristic for a $\Sigma-\Sigma$ transition of a linear molecule. Parts of the spectrum are blended by C_2 or CN electronic transitions. This is demonstrated in Fig. 3 for DC_6N; the upper part shows the $A\,^3\Sigma^- - X\,^3\Sigma^-$ electronic origin band and the lower part the same frequency region recorded under conditions that do not favor DC_6N formation.

The rotational analysis of the data was carried out using Pgopher.[34] It is expected that the molecular structure of a fairly large molecule such as HC_6N will hardly be affected upon π-electron excitation, i.e., the geometrical constants in the $A\,^3\Sigma^-$ state will not be too different from the ground-state values, $B_0''=0.028\,062\,99\ \mathrm{cm}^{-1}$ and $D_0''=10.3\times10^{-6}\ \mathrm{cm}^{-1}$.[27] More complicated is to predict the change of the spin–spin coupling constant upon excitation from the $X\,^3\Sigma^-$ ($\lambda''=0.35\ \mathrm{cm}^{-1}$, Ref. 27) to the $A\,^3\Sigma^-$ electronic state.

The ground-state values were fixed to the FTMW results and the band origin (ν_0) and rotational constant (B_0') were varied to fit the observed line positions using a standard Hamiltonian. In the case of HC_6N this gives $\nu_0=21\,208.60(5)\ \mathrm{cm}^{-1}$ and $B_0'=0.027\,92(5)\ \mathrm{cm}^{-1}$ for $T_{\mathrm{rot}}\sim25\ \mathrm{K}$[35] with a standard deviation comparable to the FWHMs of the observed lines. The values are independent of λ' with values between 0.15 and 0.65 cm^{-1}. A reasonable value for the spin–spin constant ($\lambda'=0.25\ \mathrm{cm}^{-1}$) is found by simulation of the band contour taking into account irregularities that may arise from interference of rotational lines and triplet splittings. The simulated spectrum is shown in the middle trace of Fig. 2. Acceptable fits are also found for other values of λ'. This then precludes an unambiguous assignment of the resolved rotational transitions to selected quantum states.[36] The problem is demonstrated in the lower part of Fig. 2 showing a stick diagram that covers part of the *P*-branch range: Each resolved line consists of at least three close lying components with a quantum labeling that strongly depends on λ'.

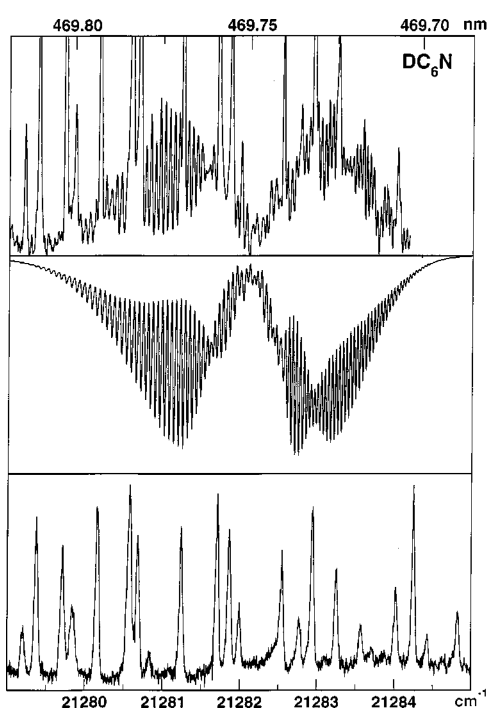

FIG. 3. The $A\,^3\Sigma^- - X\,^3\Sigma^-$ electronic origin band of DC_6N in the gas phase (upper trace). A good simulation (middle trace) is hampered as the jet spectrum is heavily blended by unrelated molecular lines, presumably C_2 or CN. The latter are shown in the lower trace, recorded under conditions that suppress DC_6N production.

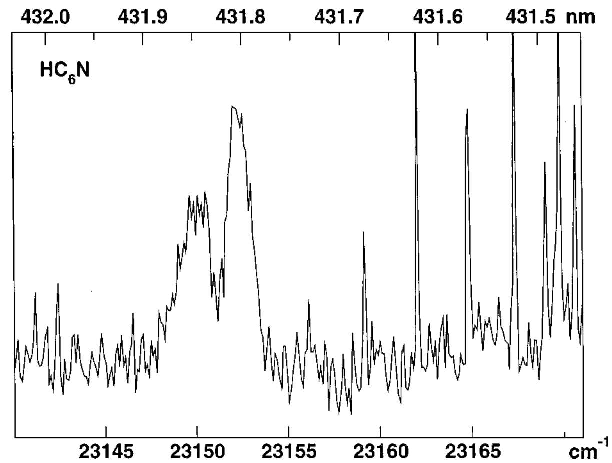

FIG. 4. The $A\,^3\Sigma^- - X\,^3\Sigma^-$ electronic transition of HC_6N involving excitation of a symmetric C≡C stretch in the upper electronic state, measured at a resolution of 0.15 cm^{-1}. The sharp lines to higher energy do not shift upon isotopic substition and are due to C_2 or CN.

In the case of DC_6N experimental ground-state constants are lacking, but neglecting zero-point effects a good estimate can be made for B_0'' starting from the microwave value[27] and the theoretically predicted equilibrium structure of HC_6N.[28] This gives $B_0''(DC_6N)=0.026\,982\ \mathrm{cm}^{-1}$. The electronic spectrum was fitted in a similar way as for HC_6N (assuming identical values for λ' and λ''). This yields $B_0'=0.026\,82(5)\ \mathrm{cm}^{-1}$ and $\nu_0=21\,282.10(5)\ \mathrm{cm}^{-1}$, showing an isotope shift of 73.5 cm^{-1} to the blue. The simulated spectrum is shown in Fig. 3.

Besides the $A\,^3\Sigma^- - X\,^3\Sigma^-$ origin band a transition involving excitation of a symmetric C≡C stretch in the upper electronic state has been observed both for HC_6N and DC_6N. The rotational contours are clearly visible as shown in Fig. 4 for HC_6N. The band positions (Table I) relative to the origin band (1943 cm^{-1} for HC_6N and 1926 cm^{-1} for DC_6N) are close to the corresponding values in the matrix (1950 and 1935 cm^{-1}, respectively).

The observed HC_6N band origin position has been compared with the diffuse interstellar band wavelengths.[37–41] The origin band is more than 50 cm^{-1} to the blue of two diffuse interstellar bands located at 21 149 and 21 151 cm^{-1}. It is concluded that HC_6N is not a carrier of one of the hitherto reported diffuse interstellar bands.

TABLE II. Comparison of the electronic, vibrational and rotational parameters of the isoelectronic HC_6N, DC_6N, and HC_7H in the gas phase and of NC_5N in a neon matrix for the $A\,^3\Sigma^- - X\,^3\Sigma^-$ (or $A\,^3\Sigma_u^- - X\,^3\Sigma_g^-$) electronic band system. All values are in cm^{-1}.

	HC_6N	DC_6N	HC_7H	NC_5N
0_0^0	21 208.60(5)[a]	21 282.10(5)[a]	19 817.92(5)[a]	22 737.3(2)[b]
ν'_{bend}	467(15)[a]	344(15)[a]	571(10)[c]	508.5(2)[b]
$\nu'_{C\equiv C}$	1942.6(2)[a]	1926.0(2)[a]	1954.46(10)[d]	1960.5(2)[b]
B''_0	0.028 062 99(2)[e]	0.026 982[f]	0.027 92[g]	⋯
B'_0	0.027 92(5)[a]	0.026 82(5)[a]	0.027 80(5)[a]	⋯
B''_0/B'_0	1.0051	1.0060	1.0043	⋯

[a]This work.
[b]Reference 42.
[c]Reference 33.
[d]Reference 13.
[e]Reference 27.
[f]Estimated from Refs. 27 and 28, this work.
[g]Reference 29.

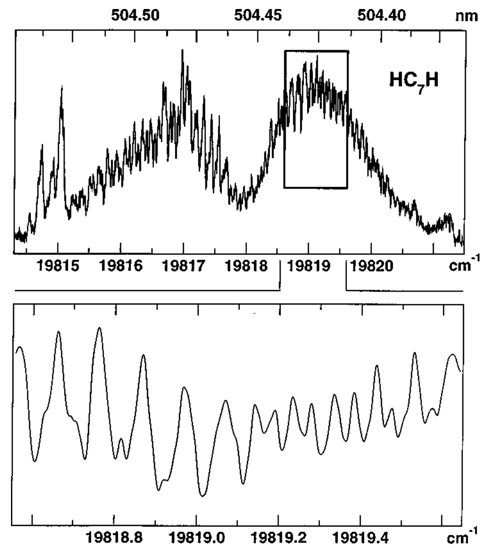

FIG. 5. The $A\,^3\Sigma_u^- - X\,^3\Sigma_g^-$ electronic origin band of HC_7H measured under Doppler free conditions (upper trace). The complex structure is due to overlapping of rotational lines with a 3:1 spin statistical alternation and J-dependent triplet splittings. The lower trace shows a zoomed spectrum of the frequency range defined by the box, demonstrating the complex structure.

C. Isoelectronic species and line broadening

HC_6N is isoelectronic with NC_5N and HC_7H. The $A\,^3\Sigma_u^- - X\,^3\Sigma_g^-$ electronic system of the latter has been observed in the gas-phase.[13] In the case of NC_5N an electronic absorption spectrum in a neon matrix[42] and computational data[43] are available, but gas-phase spectra have not been recorded. The origin band position of HC_6N is in between that of NC_5N (439.8 nm[42]) and HC_7H (504.45 nm[13]). In both cases transitions involving excitation of a symmetric C≡C stretching or bending mode have been observed with values comparable to those of HC_6N (Table II).

In Ref. 13 it was discussed that in the case of HC_7H a short lifetime of the excited electronic state causes a broadening of $\sim 0.04\ cm^{-1}$ in excess of that expected from laser resolution and Doppler width through a divergent pinhole expansion ($\sim 0.066\ cm^{-1}$). The present experiment provides a nearly Doppler free environment: For HC_6N a linewidth between 0.035 and 0.04 cm^{-1} (FWHM) is found, close to the laser bandwidth. The $A\,^3\Sigma_u^- - X\,^3\Sigma_g^-$ electronic origin band spectrum of HC_7H recorded through the planar expansion is shown in Fig. 5.[36] Indeed, transitions have been observed with $\sim 0.08\ cm^{-1}$ linewidth, but narrow lines with widths comparable to those found for HC_6N have been found as well. This suggests that the excess broadening observed in Ref. 13 might be due to unresolved triplet structures. A zoomed spectrum is shown in the lower part of Fig. 5, demonstrating the complexity of such features.

The observed spectrum has been simulated. *Ab initio* calculations predict a linear centro-symmetric structure with a ground-state rotational constant of $B''_0 = 0.027\,92\ cm^{-1}$.[29] Assuming that the spin–spin interaction in the ground state does not differ too much from that found for HC_6N a reasonable fit is obtained for $B'_0 = 0.027\,80(5)\ cm^{-1}$ and $\nu_0 = 19\,817.92(5)\ cm^{-1}$, close to the values previously obtained in Ref. 13. Again, the fit is rather independent of the exact value of λ' and a contour optimalization results in $\lambda' = 0.48\ cm^{-1}$. The ratio $B''_0/B'_0 \sim 1.005$ is comparable for HC_6N, DC_6N, and HC_7H, reflecting a slight stretch of the carbon chain upon electronic excitation (Table II).

ACKNOWLEDGMENT

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