Rotationally resolved $A^3\Sigma_u^- - X^3\Sigma_g^-$ electronic transition of NC_5N

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Abstract

The rotationally resolved $A^3\Sigma_u^- - X^3\Sigma_g^-$ electronic spectrum of the NC_5N radical has been observed in the gas phase by cavity ring down spectroscopy in a supersonic plasma. The origin band is at $v_{00} = 22832.7(1)$ cm^{-1} and a rotational analysis gives constants $B_0'' = 0.02799(4)$ and $B_0' = 0.02778(3)$ cm^{-1}. These are compared to the B_e values available from structures predicted by density functional theory and show that the molecule has a linear and centro-symmetric NCCCCCN structure. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

In recent years much progress has been achieved in the study of electronic transitions of highly unsaturated carbon chain radicals. Both matrix [1,2], gas phase [3–8] and theoretical studies [9,10] have been reported. These provide detailed spectroscopic information and allow for the first time a systematic comparison between astrophysical data in the optical range and gas phase laboratory spectra [11–14].

Of particular interest are the cyano- and isocyanopolyynes. Carbon chain radicals of the form HC_nN_m or C_nN_m are remarkably well represented among the species discovered by radio astronomy in interstellar space (e.g. [15,16]). The largest species detected so far in the interstellar medium is the linear $HC_{11}N$ chain [17]. In the laboratory rotational spectra of chains $HC_{2n+1}N$ with n as large as 8 have been recorded by Fourier transform microwave spectroscopy [18] and recently the $A^3\Sigma^- - X^3\Sigma^-$ electronic transition of HC_6N was observed in direct absorption [7]. Significantly less information is available for the dicyano derivatives. An exception is the C_5N_2 species for which optical data have been obtained in an argon matrix [19]. In this study visible absorption, laser-induced fluorescence and laser excitation spectroscopy as well as isotopic substitution were used to identify an intense absorption around 22737 cm^{-1} as due to C_5N_2. These observations strongly supported a linear centro-symmetric structure, either NCCCCCN or CNCCCNC. In recent density functional theory work the bond lengths and vibrations for these two isomers, as well as for CCNCNCC were calculated [20]. These were optimized for three electronic states: the lowest triplet state ($^3\Sigma_g^-$), the lowest open-shell singlet state ($^1\Sigma_g^-$) and the lowest closed-shell singlet state ($^1\Sigma_u^+$). From a comparison of the calculated and experimentally determined vibrational frequencies for several isotopomers it was

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concluded that C_5N_2 is linear with a centro-symmetric NCCCCCN ground state structure. The corresponding triplet and open-shell singlet states were predicted to be very close in energy with the triplet below the singlet state. In the present Letter these conclusions are confirmed from the analysis of the rotationally resolved electronic gas phase spectrum.

2. Experiment

The C_5N_2 radicals are formed by a discharge through a high pressure gas pulse (typically 100 mA at −800 V for a 10 bar backing pressure) of an 0.3% cyanogen/He mixture in the throat of a 3 cm × 300 μm multilayer slit nozzle device. The details of this nozzle and cavity ring down setup have been described before [21]. Rotational temperatures of the order of 10–30 K are routinely obtained in this way. The nozzle is mounted in an optical cavity where the expansion is intersected approximately 8 mm downstream by the pulsed light beam of a dye laser (0.035 cm^{-1} bandwidth). Typically 45 ring down events are averaged at each wavelength. The calibration has been performed using a HeI line at 438.7928 nm. This limits the accuracy with which the absolute frequency can be determined to ∼0.1 cm^{-1}.
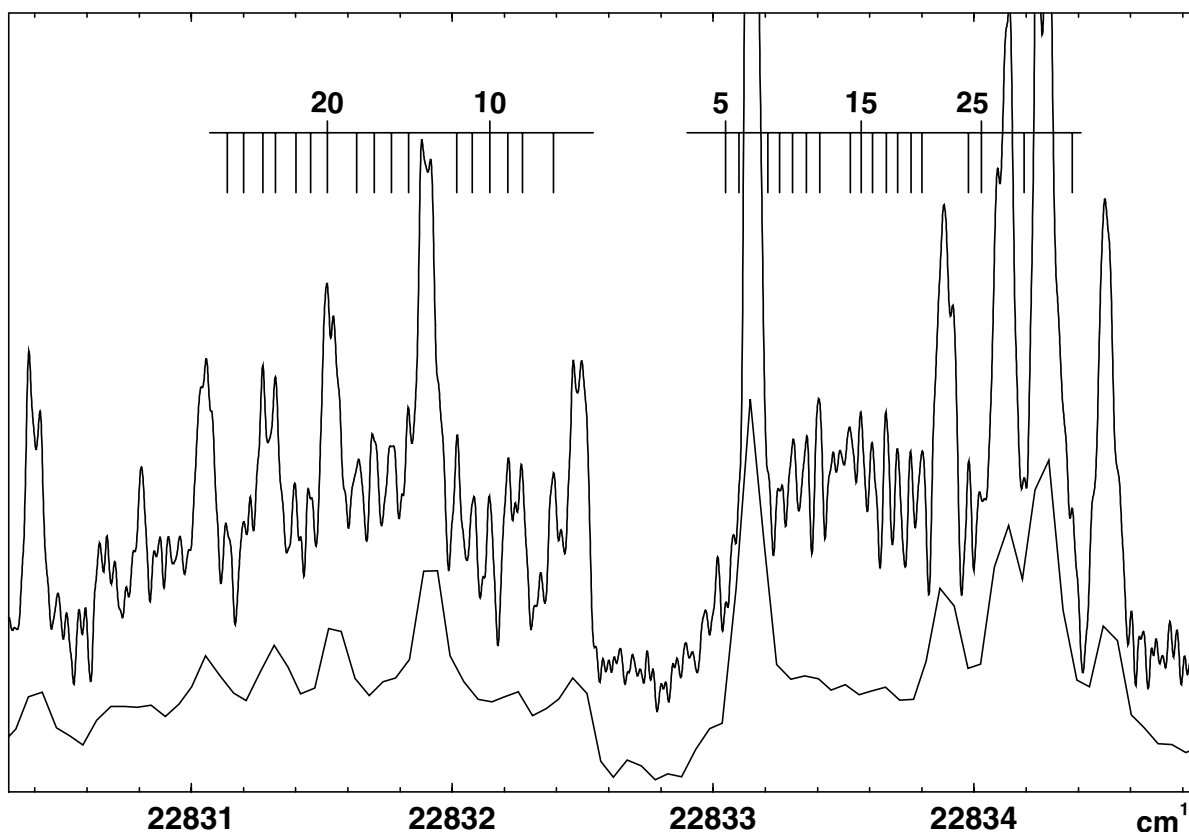

Fig. 1. In the upper trace the origin band of the $A^3\Sigma_u^- - X^3\Sigma_g^-$ electronic spectrum of C_5N_2 is shown, measured in absorption by cavity ring down spectroscopy through a supersonic planar plasma ($T_{rot} \sim 25$ K). The rotational structure is partially blended by absorption features belonging to C_2 or CN, as shown in the lower trace that is recorded at 0.15 cm^{-1} resolution under conditions that do not favour C_5N_2 formation. Nevertheless, a clear rotational progression is observable, as indicated by the solid bars, from which a linear and centro-symmetric NCCCCCN geometry is concluded (see text).

Table 1
Comparison of the experimental and theoretical spectroscopic constants for the $A^3\Sigma_u^- - X^3\Sigma_g^-$ electronic transition of NCCCCCN (cm^{-1})

	Experiment		Theory[a]		
	Ar-matrix[b]	Gas phase[c]	NCCCCCN	CNCCCNC	CCNCNCC
v_{00}	22 737.3(2)	22 832.7(1)			
v_{01}	24 697.8(2)	24 791(1)			
B_e'' $(^3\Sigma_g^-)$			0.02787	0.03014	0.03190
B_e'' $(^1\Sigma_g^-)$			0.02790	0.03019	0.03192
B_0''		0.02799(4)			
B_0'		0.02778(3)			

[a] Ref. [20].
[b] Ref. [19].
[c] This work.

3. Results

In Fig. 1 (upper trace) the rotationally resolved origin band of the $A^3\Sigma_u^- - X^3\Sigma_g^-$ electronic transition of NC_5N is shown. This spectrum resembles spectra recently recorded for the $A^3\Sigma - X^3\Sigma$ electronic transition of the iso-electronic HC_6N [7] and HC_7H [4,7] chains with origin bands around 471 and 505 nm. All these spectra show clearly resolved P and R branches, partially blended by transitions belonging to C_2 or CN, as shown in the lower trace of Fig. 1 for conditions that do not favour C_5N_2 formation. A Q branch is not present. Each rotational level is split into three fine structure levels characterized by the total angular momentum J ($J = N + 1$, N and $N - 1$, except for $N = 0$ where $J = 1$). This spin structure is not discernible but influences the rotational contour of the band system. A rotational N-numbering [1], is indicated in Fig. 1. In total 17 transitions in the P branch and 18 transitions in the R branch have been observed. [2] The absolute N assignment is hampered as transitions starting from low lying levels are not detected. In addition, a precise interpretation of the band gap requires knowledge of the spin–spin coupling constants in both electronic states, because the spin splittings are most significant for the lowest J-levels. Therefore, the num-

bering is based on the simulation of the band contour. For this λ'' was fixed to the ground state value recently determined for the iso-electronic HC_6N (0.36 cm^{-1} [22]) and λ' was optimized, yielding $\lambda' = 0.435(10)$ cm^{-1}. The rotational analysis of the observed spectrum was carried out using Pgopher [23]. The transitions were fitted using v_{00}, B_0'' and B_0' as parameters. The fit has an rms of less than 0.01 cm^{-1}. Inclusion of centrifugal distortion effects does not improve the fit. The resulting values are listed in Table 1.

The ratio B_0''/B_0' is 1.0076 and reflects a small lengthening of the chain upon electronic excitation. This value is comparable to the ratios found for the corresponding transition in HC_6N (1.0051), DC_6N (1.0060) and HC_7H (1.0043) [7]. The fit yields a band origin of $v_{00} = 22 832.7(1)$ cm^{-1}. The error is limited by the accuracy with which the absolute frequency can be determined. The band origin is ~95 cm^{-1} to the blue of the band observed in the argon matrix and ~60 cm^{-1} compared with unpublished spectra observed in a neon environment [24].

The fit can be used to determine the isomeric structure. Using the calculated bond lengths [20], B_e'' values are calculated for the NCCCCCN, the CNCCCNC and the CCNCNCC isomeric forms, in their electronic triplet and singlet states. The results are summarized in Table 1. Clearly, the present B_0'' value fits best to B_e'' calculated for the NCCCCCN isomer. Constraining B_0'' in the fit of the rotational line positions to the B_e'' value of one of the two other isomers gives significantly larger

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[1] The output of the rotational fit is largely independent of the exact values of λ'' and λ' (see [7]).

[2] A list with line positions is available on request.

rms. This comparison gives additional evidence that a linear and centro-symmetric NCCCCCN structure is responsible for the $22\,737$ cm^{-1} band observed in the argon matrix spectrum [19], rather than any of the other isomers.

The ab initio work [20] predicts the two lowest electronic states, the triplet $^3\Sigma_g^-$ and open-shell singlet $^1\Sigma_g^-$, to be very close in energy. Although the triplet state was calculated to be lower, no definite conclusion was made on the nature of the ground state. The present experiment, however, confirms the triplet character of the ground state, even though triplet splittings are not resolved. Apart from the similarities with the $A^3\Sigma$–$X^3\Sigma$ electronic transition observed for the iso-electronic HC_6N and HC_7H, it also seems to be the only way in which the lack of a 2:1 spin statistical alternation for adjacent rotational levels can be explained. Only in the case of an overlap of rotational and triplet structures a loss in intensity alternation becomes possible, assuming a centro-symmetric structure. This can also explain spectral fading, as discussed in [7]. In a singlet state, however, this effect cannot take place and consequently an alternation should have been observed.

Besides the $A^3\Sigma_u^-$–$X^3\Sigma_g^-$ origin band a transition involving excitation of a CC or CN triple bond stretching vibration in the upper electronic state (labelled 1_0^1 in [19]) has been observed. This two to three times weaker band is located in the gas phase at $24\,791(1)$ cm^{-1}. [3] This corresponds to a vibrational frequency of 1958 cm^{-1} in the upper electronic state, close to the 1961 cm^{-1} value found in the argon matrix [19].

Acknowledgements

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[3] This band is blended by a strong C_3 band and it is not possible to get a more accurate determination of the band origin.

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