Rotationally resolved $A^2\Pi_u \leftarrow X\,^2\Pi_g$ electronic transition of NC_6N^+

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The rotationally resolved $A^2\Pi_u \leftarrow X^2\Pi_g$ electronic origin band spectrum of dicyanodiacetylene cation, NC_6N^+, has been recorded in the gas phase using frequency-production double modulation spectroscopy in a liquid nitrogen cooled hollow cathode discharge and cavity ring down spectroscopy in a supersonic plasma. The analysis of the complementary results provides accurate molecular parameters for the two spin-orbit components in both electronic states. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1427710]

I. INTRODUCTION

In recent years several cyanopolyacetylene radicals (HC_nN) have been studied by Fourier transform microwave spectroscopy[1,2] and, following their laboratory detection, species as large as $HC_{11}N$ have been identified by radio astronomy in the interstellar medium.[3] The dicyano derivatives (NC_nN) may be comparably abundant in space, but are unsuitable for microwave detection due to absence of a dipole moment. In this case accurate spectroscopic information can be obtained from high resolution studies of vibrational or electronic transitions in the gas phase. The latter are available for a series of carbon chain radicals. Examples are the nonpolar NC_5N (Ref. 4) and HC_7H,[5,6] as well as chains that were already detected in dense interstellar clouds such as HC_6N (Ref. 6) and C_6H.[7] These species are formed in ion-molecule reactions and consequently spectroscopic information on carbon chain ions is needed as well, but high resolution data are rare and pure rotational spectra are limited to a few species.[8]

This is particularly true for the (di)cyanopolyacetylene cations. Electronic spectra have been recorded in neon matrices for $NC_{2n}N^+$ ($n=2–6$) and $HC_{2n+1}N^+$ ($n=2–6$).[9–12] Following these and low resolution emission studies[13–15] the rotationally resolved electronic gas phase spectrum of the cyanodiacetylene (HC_5N^+) and dicyanoacetylene (NC_4N^+)[16] as well as the cyanotriacetylene (HC_7N^+)[17] were reported. In the present work the rotationally resolved spectrum of the next larger member in the dicyano-series, NC_6N^+, is presented. The results are compared with the results of density functional theory calculations[18] and the spectroscopic parameters available for the iso-electronic chains HC_7N^+ (Ref. 17) and HC_8H^+.[19]

II. EXPERIMENT

The spectra are recorded using two complementary experimental approaches. These are frequency production double modulation (FPM) spectroscopy of a static plasma generated in a discharge cell ($T_{rot} \sim 150$ K) and cavity ring-down (CRD) spectroscopy sampling a supersonic planar

plasma ($T_{rot} = 15$ K), yielding spectra with significantly different rotational profiles. Both experimental techniques have been described. In the FPM experiment[20] mixtures of 0.5%–0.6% cyanogen/He are discharged in a liquid nitrogen cooled hollow cathode incorporated into a White-type multiple reflection cell ($L_{tot} \sim 100$ m). Production modulation is obtained by applying a rectified 17 kHz ac voltage (-500 to 700 V). The laser beam is electro-optically modulated at a radio frequency of 192 MHz and detected by a fast photodiode. Subsequent phase sensitive demodulation of the high frequency portion of the signal during a production cycle gives absorption bands that have a derivativelike shape. The resolution is Doppler limited and typically of the order of 550 MHz.

In the CRD setup[21] the NC_6N^+ radicals are formed by a discharge through a high pressure gas pulse (typically 100 mA at -1000 V for a 12 bar backing pressure) of an 0.2% cyanogen/He mixture in the throat of a 3 cm×300 μm multilayer slit nozzle device. A standard CRD spectrometer is used to detect the signals in direct absorption. The resolution is limited by the bandwidth of the laser to ~ 0.035 cm^{-1}. In both experiments iodine spectra are used for an absolute frequency calibration.

III. RESULTS AND DISCUSSION

An overview scan of the $A^2\Pi_u \leftarrow X^2\Pi_g$ electronic origin band transition of NC_6N^+ recorded by FPM in the discharge cell is shown in Fig. 1. In the range 15 240–15 248 cm^{-1} approximately 200 individual absorption lines are resolved. These transitions belong to the P-, Q- and R-branches of two subbands corresponding to the parallel $A^2\Pi_{3/2} \leftarrow X^2\Pi_{3/2}$ and $A^2\Pi_{1/2} \leftarrow X^2\Pi_{1/2}$ electronic transitions. The intensity ratio of the two bands is determined by the "spin-orbit temperature" and the value of the spin-orbit splitting (A'') in the ground state. The latter is estimated from previous studies to be of the order of $-40(5)$ cm^{-1},[16] the minus indicating that the $\Omega = \frac{3}{2}$ spin-orbit component is lower in energy than the $\Omega = \frac{1}{2}$. At the high ambient temperature in the cell both spin-orbit components are equally intense. The rotational population is distributed over many levels and the intensity of both Q-branches and transitions starting from low J-levels is low. Clear band heads, however, are missing. Moreover, the spin-

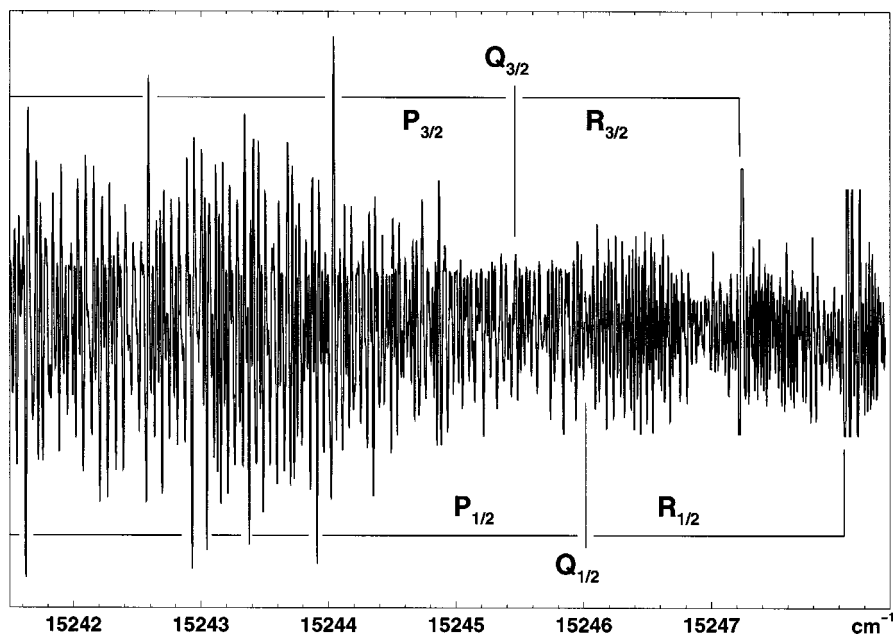a)Electronic mail: Henricus.Linnartz@unibas.ch

FIG. 1. Rotationally resolved frequency production double modulation absorption spectrum of the $A^2\Pi_u \leftarrow X^2\Pi_g$ electronic origin band of NC_6N^+ measured in a liquid-nitrogen cooled hollow cathode discharge ($T_{rot} \sim 150$ K). The P-, Q- and R-branches of the $A^2\Pi_{3/2} \leftarrow X^2\Pi_{3/2}$ and $A^2\Pi_{1/2} \leftarrow X^2\Pi_{1/2}$ subbands are indicated.

orbit components overlap as the difference in spin-orbit splittings in ground and excited state, ΔA, appears to be small. All these factors together lead to ambiguity in the assignment of the rotational lines. What is missing is a clearly defined starting point. This is provided by the jet spectrum.

In Fig. 2 part of the spectral region of Fig. 1 is shown. The spectrum is recorded by CRD in the plasma expansion. Only the lower subband, $A^2\Pi_{3/2} \leftarrow X^2\Pi_{3/2}$, is clearly visible now, as the population of the upper spin-orbit component is low. Besides unresolved P- and R-branches,[22] a clear Q-branch is observed starting at $15\,245.46(3)$ cm^{-1}. This branch is not visible in Fig. 1, but the CRD position allows the assignment of transitions belonging to the $A^2\Pi_{3/2} \leftarrow X^2\Pi_{3/2}$ subband within ± 1 J quantum numbering in the FPM spectrum. The band gap is $\sim 10B$ [with $B \sim 0.019$ cm^{-1} (Ref. 18)] reflecting that the lowest rotational transitions correspond to $P(\frac{5}{2})$ and $R(\frac{3}{2})$. Adjacent transitions are separated by $\sim 2B$. In this way more than 80(40) transitions have been assigned in $P(R)$-branch of the $A^2\Pi_{3/2} \leftarrow X^2\Pi_{3/2}$ band with J-values up to 90.5.[23] These values are then fitted with PGopher[24] using ν_0, B_0'', B_0', D_0'' and D_0' as variables yielding a rms of 0.002 cm^{-1}. The resulting constants are listed in Table I. The value for $B_0'' = 0.018\,753\,3(55)$ cm^{-1} is close to the B_e-value of $0.018\,67$ cm^{-1} as obtained from density functional calculations.[18] A simulation using these constants proves that the stronger feature in Fig. 1 at $15\,247.23(3)$ cm^{-1} corresponds to the R-branch band head of the $A^2\Pi_{3/2} \leftarrow X^2\Pi_{3/2}$ system. A similar feature is observed at $15\,247.85$ cm^{-1} and is tentatively assigned to the R-branch band head of the second spin-orbit system.

The lines that are left over are mainly due to the $\Omega = \frac{1}{2}$
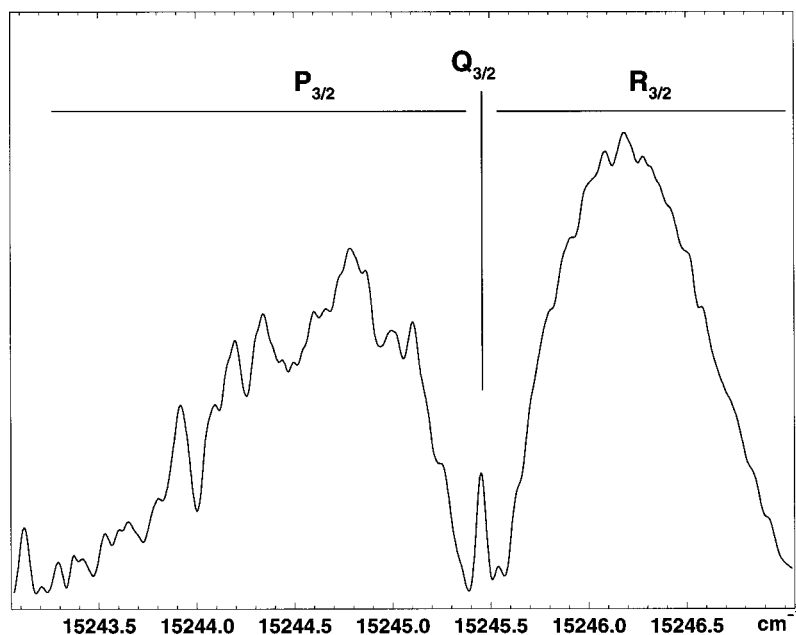

FIG. 2. Cavity ring down absorption spectrum of the $A^2\Pi_{3/2} \leftarrow X^2\Pi_{3/2}$ electronic origin band of NC_6N^+, recorded through a supersonic plasma. The second spin-orbit component is not visible at the low temperature in the jet ($T_{rot} \sim 15$ K). The Q-branch position is used to assign the FPM spectrum.

TABLE I. Molecular constants (in cm^{-1}) for the $A^2\Pi_{3/2}-X^2\Pi_{3/2}$ and for the $A^2\Pi_{1/2}-X^2\Pi_{1/2}$ electronic origin band transition of NC$_6$N$^+$. The molecular parameters for the $A^2\Pi_u\leftarrow X^2\Pi_g$ electronic origin band transition of the iso-electronic HC$_7$N$^+$ (Ref. 17) and HC$_8$H$^+$ (Ref. 19) species are listed for comparison.

	NC$_6$N$^+$		HC$_7$N$^+$	HC$_8$H$^+$
	$\Omega=3/2$	$\Omega=1/2$	$\Omega=3/2$	$\Omega=3/2$ and $1/2$
B_0''	0.018 753 3(55)	0.018 707(19)	0.018 966 5(71)	0.019 077 9(93)
D_0''	6.7(15).10^{-9}	6.2(38).10^{-9}		
B_0'	0.018 558 5(56)	0.018 565(19)	0.018 773 1(72)	0.018 867 3(94)
D_0'	7.1(16).10^{-9}	8.3(39).10^{-9}		
ΔB	-0.00019	-0.00014	-0.00019	-0.00021
ΔA	$+0.56$		-2.04	-3.00
ν_0	15 245.737(1)		14 925.423(4)	14 143.1815(5)

component. The rotational assignment is problematic now as information on the Q-branch of the $A^2\Pi_{1/2}\leftarrow X^2\Pi_{1/2}$ band is missing. The difference between the band heads, however, indicates that the $Q_{1/2}$-branch is expected around 15 246.1 cm^{-1}. In addition, only minor differences between the rotational constants for the two spin-orbit systems are expected. In previous studies transitions originating from different spin-orbit components were fitted with one single set of rotational parameters.[7,16,19] In the present experiment this turns out not to be possible. However, as long as the effect of spin uncoupling is small, i.e., $2BJ \ll |A|$, B is best replaced by effective parameters $B_{\text{eff}}(^2\Pi_{1/2})$ and $B_{\text{eff}}(^2\Pi_{3/2})$. In second order perturbation theory the difference ΔB_{eff} is given by

$$\Delta B_{\text{eff}} = \frac{2B^2}{\bar{A}}, \tag{1}$$

where $\bar{A} = A - 2B$.[25] A is expected to be of the order of $-40(5)$ cm^{-1} (Ref. 16) which puts an additional constraint to the fit. The line positions and most likely assignment for

transitions belonging to the $A^2\Pi_{1/2}\leftarrow X^2\Pi_{1/2}$ system are available from (Ref. 26). The resulting molecular parameters are given in Table I. The quality of the fit will be worse as only a few transitions share a common level (rms ~ 0.004 cm^{-1}).[26] Nevertheless, using Eq. (1) an A''-value between -15 and -32 cm^{-1} is calculated.[27] The simulation confirms that the band head position coincides with the feature at 15 247.85 cm^{-1}.

The spectral features of NC$_6$N$^+$ are expected to be qualitatively similar to those of the iso-electronic cyanotriacetylene cation[17] and tetraacetylene cation.[19] The molecular parameters of the $A^2\Pi_u\leftarrow X^2\Pi_g$ electronic origin bands of these two ions are listed in Table I as well. These bands are shifted to lower energy, by 320 cm^{-1} for HC$_7$N$^+$ and by 1103 cm^{-1} for HC$_8$H$^+$. The ΔA value of HC$_7$N$^+$ (-2.04 cm^{-1}) is comparable to that of HC$_8$H$^+$ (-3.00 cm^{-1}), but the corresponding value for NC$_6$N$^+$ is significantly smaller and, moreover, is positive ($+0.56$ cm^{-1}). This value, however, is very close to the $\Delta A = +0.53$ cm^{-1} found for NC$_4$N$^+$.[16] There it was concluded that this anomaly is due to a spin-orbit induced interaction of the upper $A^2\Pi_{1/2}$ electronic state with another low lying electronic state, presumably of $^2\Sigma$ character, whereas the $A^2\Pi_{3/2}$ state is not affected. This becomes clear from the different values for $\Delta B = B_0' - B_0''$: for the $\Omega = \frac{3}{2}$ component a value of 0.000 19 cm^{-1} is found, similar to the values determined for HC$_7$N$^+$ (0.000 19 cm^{-1}) and HC$_8$H$^+$ (0.000 21 cm^{-1}), but for $\Omega = \frac{1}{2}$ the value decreases to 0.000 14 cm^{-1}. The second-order spin-orbit contribution to the rotational constant for a Π state is given by[28,29]

$$B^{(2)} = \Sigma_{n \neq 0} \frac{4B^2}{E_0^0 - E_n^0}. \tag{2}$$

With $|\Delta E| = 40$ cm^{-1} this gives $B^{(2)} \sim 0.000 04$ cm^{-1}, i.e., an unperturbed value for ΔB of 0.000 18 cm^{-1}, close to the value of the other spin-orbit component.

In the case of NC$_4$N$^+$ it was also found that the $^2\Sigma - ^2\Pi$ interaction removes the degeneracy of the e- and
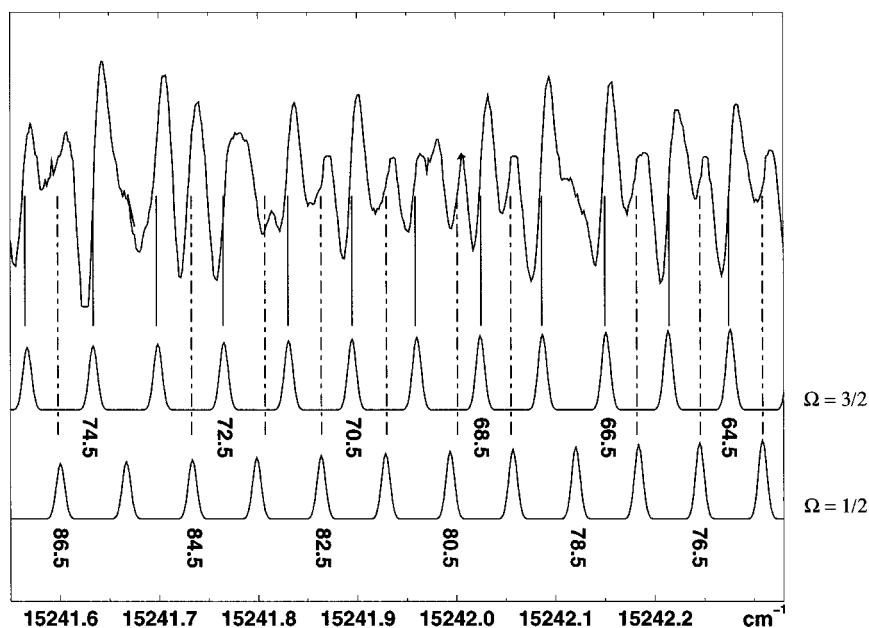

FIG. 3. High J-level transitions with their typical $1f$ derivative line shapes recorded in the FPM experiment. The simulated spectrum is shown for both spin-orbit components. There is no evidence for Λ-doubling (see the text).

f-symmetry, resulting in a resolvable Λ-doubling. This effect is not observed here. In Fig. 3 part of the P-branch range for high J-levels in both spin-orbit components is shown. The simulated spectrum is given as well. Clearly, there is no evidence for Λ-doubling within the experimental resolution: the size of the splitting would have been J-dependent and the expected 2:1 spin-statistical alternation is lacking. This is also expected: the rotational constant of NC_6N^+ is 2.5 times smaller than that of NC_4N^+ (~ 0.044 cm^{-1}) and since the Λ-type doubling constants p and q are proportional to B and B^2, respectively, splittings will be considerably smaller.

ACKNOWLEDGMENTS

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[23] See EPAPS Document No. E-JCPSA6-116-004204 for a list with line positions and observed-calculated values. This document may be retrieved via the EPAPS homepage (http://www.aip.org/pubserv/epaps.html) or from ftp.aip.org in the director /epaps/. See the EPAPS homepage for more information.

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