Rotationally resolved $A^2\Pi_{u} \leftarrow X^2\Pi_{g}$ electronic transition of NC$_6$N$^+$

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The rotationally resolved $A^2\Pi_{u} \leftarrow X^2\Pi_{g}$ electronic origin band spectrum of dicyanodiacetylene cation, NC$_6$N$^+$, 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$_n$N) have been studied by Fourier transform microwave spectroscopy and, following their laboratory detection, species as large as HC$_{11}$N have been identified by radio astronomy in the interstellar medium. The dicyano derivatives (NC$_n$N) 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$_3$N (Ref. 4) and HC$_2$H, as well as chains that were already detected in dense interstellar clouds such as HC$_6$N (Ref. 6) and C$_6$H. 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.

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$^+$ ($n = 2–6$), following these and low resolution emission studies the rotationally resolved electronic gas phase spectrum of the cyanodiacetylene (HC$_5$N$^+$) and dicyanacetylene (NC$_4$N$^+$) as well as the cyanatriacetylene (HC$_7$N$^+$) were reported. In the present work the rotationally resolved spectrum of the next larger member in the dicyano-series, NC$_6$N$^+$, is presented. The results are compared with the results of density functional theory calculations and the spectroscopic parameters available for the iso-electronic chains HC$_5$N$^+$ (Ref. 17) and HC$_8$H$^+$.

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$_{\text{wall}} \approx 150$ K) and cavity ring-down (CRD) spectroscopy sampling a supersonic planar plasma (T$_{\text{wall}} \approx 15$ K), yielding spectra with significantly different rotational profiles. Both experimental techniques have been described. In the FPM experiment mixtures of 0.5%–0.6% cyanogen/He are discharged in a liquid nitrogen cooled hollow cathode incorporated into a White-type multiplet reflection cell ($L_{\text{cell}} \approx 100$ 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 derivative-like shape. The resolution is Doppler limited and typically of the order of 550 MHz.

In the CRD setup the NC$_6$N$^+$ 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$_6$N$^+$ recorded by FPM in the discharge cell is shown in Fig. 1. In the range 15240–15248 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 ($A^\pi$) in the ground state. The latter is estimated from previous studies to be of the order of $-40(5)$ cm$^{-1}$, the minus indicating that the $\Omega = 3/2$ spin-orbit component is lower in energy than the $\Omega = 1/2$. 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-
orbit components overlap as the difference in spin-orbit splittings in ground and excited state, $\Delta A$, 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, $A^2\Pi_{3/2} - X^2\Pi_{3/2}$, is clearly visible now, as the population of the upper spin-orbit component is low. Besides unresolved $P$- and $R$-branches, 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 $A^2\Pi_{3/2} - X^2\Pi_{3/2}$ subband within $\pm J$ 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 $P(\frac{1}{2})$ 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 $A^2\Pi_{3/2} - X^2\Pi_{3/2}$ band with $J$-values up to $90.5$. These values are then fitted with PChoper using $v_0$, $B_0^a$, $B_0'$, $D_0^a$ and $D_0'$ as variables yielding a rms of $0.002$ cm$^{-1}$. The resulting constants are listed in Table I. The value for $B_0^a = 0.0187533(55)$ cm$^{-1}$ is close to the $B_e$-value of $0.01867$ cm$^{-1}$ as obtained from density functional calculations. 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 $A^2\Pi_{3/2} - X^2\Pi_{3/2}$ 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 $\Omega = \frac{1}{2}$
component. The rotational assignment is problematic now as information on the \( Q \)-branch of the \( A^2 \Pi_{1/2} \rightarrow X^2 \Pi_{1/2} \) 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 \( \Delta B_{\text{eff}} \) is given by
\[
\Delta B_{\text{eff}} = \frac{2B^2}{\bar{A}},
\]
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 \( A^2 \Pi_{1/2} \rightarrow X^2 \Pi_{1/2} \) 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 \( \sim 0.004 \) cm\(^{-1}\)).\(^{26}\) Nevertheless, using Eq. (1) an \( A^\prime \)-value between \(-15 \cdots -32\) 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\(^7\) and tetracetylene cation.\(^{19}\) The molecular parameters of the \( A^2 \Pi_u \rightarrow X^2 \Pi_g \) 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\(_9\)H\(^+\). The \( \Delta \Delta \) value of HC\(_7\)N\(^+\) (\(-2.04\) cm\(^{-1}\)) is comparable to that of HC\(_9\)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 \( \Delta \Delta = +0.53\) cm\(^{-1}\) found for NC\(_6\)N\(^+\).\(^{16}\) 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 \( \Sigma \) 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\(_9\)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 \( \Pi \) state is given by\(^{28,29}\)

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

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

In the case of NC\(_6\)N\(^+\) it was also found that the \( \Sigma_{-}\Pi \) 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 A-doubling (see the text).](image-url)

### Table I. Molecular constants (in cm\(^{-1}\)) for the \( A^2 \Pi_{1/2} \rightarrow X^2 \Pi_{1/2} \) and for the \( A^2 \Pi_{1/2} \rightarrow X^2 \Pi_{3/2} \) electronic origin band transition of NC\(_6\)N\(^+\).

<table>
<thead>
<tr>
<th></th>
<th>NC(_6)N(^+)</th>
<th>HC(_7)N(^+)</th>
<th>HC(_9)H(^+)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Omega = 3/2 )</td>
<td>( B') 0.018 753 5(55)</td>
<td>0.018 707(19)</td>
<td>0.018 966 5(71)</td>
</tr>
<tr>
<td></td>
<td>( B'') 6.2(15).10(^{-9})</td>
<td>6.2(38).10(^{-9})</td>
<td>0.019 077 9(93)</td>
</tr>
<tr>
<td>( \Omega = 1/2 )</td>
<td>( B') 0.018 755 7(6)</td>
<td>0.018 565(19)</td>
<td>0.018 773 1(72)</td>
</tr>
<tr>
<td></td>
<td>( B'') 8.3(16).10(^{-9})</td>
<td>8.3(39).10(^{-9})</td>
<td>0.018 673 9(94)</td>
</tr>
<tr>
<td>( \Delta B )</td>
<td>-0.000 19</td>
<td>-0.000 14</td>
<td>-0.000 19</td>
</tr>
<tr>
<td>( \nu_0 )</td>
<td>15 245.737(1)</td>
<td>14 925.423(4)</td>
<td>14 143.1815(5)</td>
</tr>
</tbody>
</table>
Acknowledgments

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22 No rotational resolution has been obtained, presumably because of residual Doppler broadening.
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.
24 C. M. Western, School of Chemistry, University of Bristol, UK, PGOPHER, 1994 and 1998.
26 See Ref. 23.
27 Shifting the rotational assignment by ±1 J gives values of −7 and −115 cm⁻¹.
29 R. F. Curl, Mod. Phys. 9, 585 (1965).