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# Millimetre- and submillimetre-wave spectroscopy of $^{13}C$ and $^{15}N$ isotopomers of cyanoacetylene, HCCCN, in the ground and vibrationally excited states†

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The pure rotational spectra of the astrophysically important monosubstituted $HC_3N$-isotopomers $HCC^{13}CN$, $HC^{13}CCN$, $H^{13}CCCN$ and $HCCC^{15}N$ in their ground and various vibrationally excited states, which will be denoted ($v_4$, $v_5$, $v_6$, $v_7$) hereafter, have been studied extensively in the 2 mm region. Transitions of the ground vibrational states and vibrational satellites appendant to the two lowest bending fundamentals $v_6$ and $v_7$ have been measured up to 625 GHz. The Fermi resonance system (0,1,0,0)/(0,0,0,3) has been analyzed for the $HCC^{13}CN$ and $H^{13}CCCN$ isotopomers for the first time. Furthermore, pure rotational transitions of the four doubly substituted isotopomers $HC^{13}C^{13}CN$, $H^{13}CC^{13}CN$, $H^{13}C^{13}CCN$ and $HCC^{13}C^{15}N$ could be detected for the first time, not only in the ground but also in vibrationally excited states. This work is to provide accurate the astronomical community.

## 1. Introduction

The cyanopolyynes $HC_nN$ ($n = 1, 3, 5, \ldots$) belong to the most prominent classes of interstellar molecules. In the interstellar medium (ISM), chains up to $n = 11$ have been detected.[1] Because of low-lying bending vibrations, cyanopolyynes can be found in the interstellar and circumstellar media, not only in the ground but also in vibrationally excited states: vibrationally excited HCN was first detected by Ziurys and Turner,[2] vibrationally excited $HC_3N$ by Clark *et al.*[3] and very recently Thorwirth *et al.*[4] detected vibrationally excited $HC_5N$ in its first excited bending states $v_{10}$ and $v_{11}$; toward the protoplanetary nebula CRL 618.

Recently, we reported on the investigation of the millimetre- and submillimetre-wave spectrum of the main isotopomer of cyanoacetylene, HCCCN.[5] In the case of cyanoacetylene not only the main isotopomer but also the $^{13}C$ and $^{15}N$ isotopomers are of astrophysical interest, both in their ground and vibrationally excited states. In 1999, Wyrowski *et al.*[6] reported on the first astronomical detection of $^{13}C$ isotopomers in their (0,0,1,0), (0,0,0,1) and (0,0,0,2) vibrational states in hot molecular cores associated with ultra-compact H II regions.

There is only little laboratory data on $HC_3N$-isotopomers available in the literature. Investigations on isotopomers in their ground vibrational states have been reported by Westenberg and Wilson,[7] Johnson and Lovas,[8] Creswell *et al.*,[9] Lafferty and Lovas[10] and Mallinson and de Zafra.[11] The latter work also marks the only previous study on vibrationally excited $HC_3N$ isotopomers providing the data Wyrowski *et al.*[6] used for their astronomical identifications. However, this laboratory investigation was restricted to a frequency range from 26.5 to 40 GHz and therefore only one to two rotational transitions per vibrational state were observed. Deuterated cyanoacetylene ($DC_3N$) has been studied in the ground and various vibrationally excited states by Mallinson and de Zafra[11] and Plummer *et al.*[12] A diode laser investigation of the $\nu_2$ band of $HCC^{13}CN$ has been reported by Yamada and Winnewisser,[13] but this stretching mode corresponds to an energy of approximately 2232 $cm^{-1}$ which is too high to be of astrophysical importance. An investigation on direct *l*-type transitions of $HCCC^{15}N$ has been performed by Haekel and Mäder.[14]

The measurements presented here were carried out in order to extend the currently available information on rotational spectra of $HC_3N$ isotopomers to provide improved rest frequencies for the astronomical community.

## 2. Experimental

The $^{13}C$ enriched sample of $HC_3N$ was obtained *via* dc glow discharge of acetylene, $C_2H_2$, and $H^{13}CN$, which itself was synthesized from $K^{13}CN$ following the procedure of King and Nixon.[15] The product was trapped and stored under liquid nitrogen. The discharge leads mainly to the formation of $HCC^{13}CN$. Nevertheless, one obtains also an enrichment of $^{13}C$ in the remaining positions making the discharge the preferable method of synthesis for the present investigation in comparison with conventional synthetic routes. For the measurements, the sample tube was kept at approximately −80 °C, and the probe was introduced to a 3.5 m free space absorption cell kept at room temperature. The measurements were carried out at total pressures from 0.5 to 3 Pa employing primarily the enriched sample. Additionally, some lines of $^{13}C$ isotopomers were recorded in natural abundance. $HCCC^{15}N$ was investigated in natural abundance exclusively. A fresh sample was introduced into the cell every 30 min to 3 h.

In the 2 mm (118–178 GHz) region, a KVARZ (Nishnii Novgorod, Russia) frequency synthesizer was used. Submillimetre (submm) spectra were recorded using the Cologne Terahertz Spectrometer[16,17] with its phase stabilized backward wave oscillators (BWOs, ISTOK Reasearch and Production Company, Moscow region, Russia)[18] as sources and a

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† Electronic Supplementary Information available. See http://www.rsc.org/suppdata/cp/b0/b009743h/

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magnetically tuned, liquid-He-cooled InSb hot electron bolometer as detector.

## 3. Observed spectra, analyses and discussion

Initial data were collected by recording continuous frequency spans of 2 to 3.5 GHz in the 2 mm range enfolding every single $J$ of a given isotopomer to obtain its ground state transition as well as a plethora of vibrational satellite lines. In the submm region, selected lines were recorded. A total of 1037 lines have been newly collected for all isotopomers. Typical uncertainties for strong lines are of the order of 10–20 kHz. For higher energetic states and for lines measured in natural abundance they may be as large as 300 kHz.

The theory of linear molecules in vibrationally excited states has been worked out, *e.g.*, by Yamada *et al.*[19] in the past. Very recently, Okabayashi *et al.*[20] have summarized theoretical aspects comprehensively in a work on the related linear molecule $FC_3N$. These two publications should be referred to for a detailed insight into the theoretical background.

Tables S1–S8 containing the experimental transition frequencies obtained in the present investigation are available as Electronic Supplementary Information.† The data were fitted using Bizzocchi's program LMFIT[21] which is based on the treatment by Yamada *et al.*,[19] taking into account previously published data.[8–11] All parameters are defined positively except for the quartic centrifugal distortion constant $D$. Uncertainties of the parameters are given in parentheses as 1$\sigma$ in units of the least significant digits and refer to a reduced standard deviation of 1. The molecular parameters derived are shown in Tables 1–8.

### 3.1. Monosubstituted isotopomers

**3.1.1. $HCC^{13}CN$.** In the case of $HCC^{13}CN$ vibrational satellites corresponding to states up to ~1500 $cm^{-1}$ could be identified including the following states: (0,0,0,1), (0,0,0,2), (0,0,0,3), (0,0,0,4), (0,0,0,5), (0,0,0,6), (0,0,0,7), (0,0,1,0), (0,0,2,0), (0,1,0,0), (0,2,0,0), (1,0,0,0), (0,0,1,1), (0,0,1,2), (0,1,0,1), (0,1,0,2) and (1,0,0,1). However, we would like to concentrate in the present context on the (0,0,0,1), (0,0,0,2), (0,0,1,0) vibrational states which have been detected already in space along with the (0,0,1,1), (1,0,0,0) and (1,0,0,1) vibrational states and the Fermi resonance system (0,1,0,0)/(0,0,0,3) all of which are lying higher in energy.

The molecular constants of $HCC^{13}CN$ obtained in the present investigation are given in Table 1. In the fit of the (0,0,0,2) vibrational state a peculiarity occurred: generally, corrected values for the vibrational dependence of the $l$-type doubling constant $q_7$ and its centrifugal distortion corrections $q_{7J}$ and $q_{7JJ}$ for the parent molecule $HC_3N$[5] and the isotopomers presented here were obtained by increasing the magnitude of the corresponding values of the (0,0,0,1) states by 0.4, 4 and 20%, respectively. For $HCC^{13}CN$ this strategy was found to yield unsatisfactory results. Smaller values for

Table 1 Molecular constants (MHz) of $HCC^{13}CN$

| Parameter | (0,0,0,0) | (1,0,0,0) | (1,0,0,1) |
|---|---|---|---|
| $B_v$ | 4530.197 762(97) | 4524.062 07(19) | 4538.773 73(10) |
| $D_v \times 10^3$ | 0.541 639(38) | 0.588 64(32) | 0.646 95(17) |
| $H_v \times 10^9$ | 0.0427(45) | | |
| $q_t$ | | | 6.709 15(20) |
| $q_{tJ} \times 10^6$ | | | −34.37(35) |
| | (0,0,1,0) | (0,0,0,1) | (0,0,0,2) |
| $B_v$ | 4539.183 507(71) | 4544.387 513(73) | 4558.578 149(75) |
| $D_v \times 10^3$ | 0.551 336(31) | 0.565 103(31) | 0.589 247(24) |
| $H_v \times 10^9$ | 0.0639(38) | 0.1003(38) | 0.1481(28) |
| $q_t$ | 3.627 971(97) | 6.528 44(15) | 6.554 55[a] |
| $q_{tJ} \times 10^6$ | −2.161(14) | −16.140(61) | −16.786[a] |
| $q_{tJJ} \times 10^{12}$ | | 59.3(76) | ←[b] |
| $x_L \times 10^{-3}$ | | | 20.869 93(18) |
| $d_{JL} \times 10^3$ | | | −15.955(19) |
| $h_{JL} \times 10^6$ | | | 0.0177(33) |
| | (0,1,0,0) | (0,0,0,3) | (0,0,1,1) |
| $B_v$ | 4531.750 932(60) | 4572.726 852(81) | 4553.474 595(36) |
| $D_v \times 10^3$ | 0.543 206 1(97) | 0.613 457(31) | 0.574 326(23) |
| $H_v \times 10^9$ | 0.045[c] | 0.1934(35) | 0.1141(34) |
| $q_t$ | 2.519 073(98) | 6.574 260(50) | [d] |
| $q_{tJ} \times 10^6$ | −1.401(18) | −16.879(10) | [d] |
| $q_{tJJ} \times 10^9$ | | 0.06[c] | [d] |
| $x_L \times 10^{-3}$ | | 20.688 87(44) | 17.2465(40) |
| $d_{JL} \times 10^3$ | | −17.068(12) | 65.196(73) |
| $h_{JL} \times 10^6$ | | −0.0999(34) | 11.64(29) |
| $l_{JL} \times 10^9$ | | | −0.153(26) |
| $r_{67} \times 10^{-3}$ | | | −12.7743(61) |
| $r_{67J} \times 10^3$ | | | −14.806(60) |
| $r_{67JJ} \times 10^6$ | | | −3.193(82) |
| $u_{67} \times 10^6$ | | | 2.897(80) |
| $\Delta E_{(0,1,0,0)-(0,0,0,3)}$ | 133 089.26(47) | | |
| $F_0$ | 1119.12(26) | | |
| $F_{0J} \times 10^3$ | −64.002(82) | | |

[a] Estimated value to account for vibrational dependence of the parameter, see text Section 3.1.1. [b] Not corrected for vibrational dependence. Constrained to the value $q_{7JJ}$ of (0,0,0,1), see text Section 3.1.1. [c] Kept fixed in the analysis. [d] Constrained to the values $q_7$, $q_{7J}$, $q_{7JJ}$, $q_6$ and $q_{6J}$ of (0,0,0,1) and (0,0,1,0), respectively.

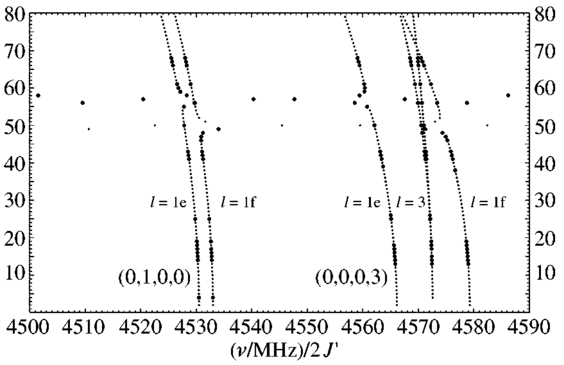

**Fig. 1** Fortrat diagram of the (0,1,0,0)/(0,0,0,3) Fermi resonance system of HCC$^{13}$CN. The upper rotational quantum number $J'$ has been plotted against the reduced frequency $\nu_{\mathrm{red}} = \nu_{(J'-J'')}/2J'$. Filled circles (●) denote the experimental values. Small dots (·) indicate calculated values based on the current parameter sets. The crossings of both the substates 1f and 1e at $J = 49$ and $J = 56$, respectively, are clearly apparent.

$q_{7JJ}$ yielded a much better standard deviation. Therefore, $q_{7JJ}$ of the (0,0,0,1) vibrational state has also been employed for the (0,0,0,2) state of HCC$^{13}$CN. This effect may be due to a weak Coriolis resonance between the (0,0,1,0) and (0,0,0,2) states being non-negligible in the present data set.[22] Promising trial fits have been performed for the parent species HC$_3$N with its larger data set, but the set still seems to be too small to yield unambiguous results. Accordingly, a Coriolis resonance may also occur between the (0,0,1,1) and (0,0,0,3) states. This effect may be revealed by the comprehensive set of parameters needed in the present analysis of the (0,0,1,1) vibrational state. However, to get certainty about these effects additional data is needed.

For the (1,0,0,0) and (1,0,0,1) vibrational states, effective fits have been performed since the inclusion of the corresponding resonant states was beyond the aim of the present study. These states were investigated in the 2 mm region exclusively.

Selected transitions of the (0,1,0,0)/(0,0,0,3) Fermi resonance system were recorded up to 622 GHz enabling the observation of both crossings of the $l$ = 1f substate at $J = 49$ and $l$ = 1e substate at $J = 56$, respectively. Eight transitions of this system have been treated as cross ladder transitions, four of which originate either from the (0,1,0,0) or the (0,0,0,3) vibrational state (see Table S1).† A Fortrat diagram of this system is shown in Fig. 1. The observation of perturbed transitions for both vibrational states permitted a very accurate determination of the energy difference $\Delta E$, the Fermi interaction term $F_0$ and its centrifugal distortion correction $F_{0J}$. The energy difference found for HCC$^{13}$CN is much larger with respect to

**Table 2** Molecular constants (MHz) of HC$^{13}$CCN

| Parameter | (0,0,0,0) | (0,1,0,0) | (0,0,1,0) |
|---|---|---|---|
| $B_v$ | 4529.760 527(77) | 4531.316 05(20) | 4538.840 222(76) |
| $D_v \times 10^3$ | 0.541 434(37) | 0.542 81(27) | 0.551 433(31) |
| $H_v \times 10^9$ | 0.0454(48) | | 0.0594(38) |
| $q_t$ | | 2.521 55(15) | 3.597 19(10) |
| $q_{tJ} \times 10^6$ | | | −2.093(15) |
| | (0,0,0,1) | (0,0,0,2) | (0,0,1,1) |
| $B_v$ | 4543.781 830(97) | 4557.806 909(87) | 4552.953 58(17) |
| $D_v \times 10^3$ | 0.564 518(40) | 0.588 301(29) | 0.574 46(30) |
| $H_v \times 10^9$ | 0.0948(49) | 0.1473(33) | |
| $q_t$ | 6.575 91(19) | 6.602 21$^a$ | $^b$ |
| $q_{tJ} \times 10^6$ | −16.322(80) | −16.976$^a$ | $^b$ |
| $q_{tJJ} \times 10^{12}$ | 78.7(97) | 94.4$^a$ | $^b$ |
| $x_L \times 10^{-3}$ | | 20.221 84(20) | 16.2031(25) |
| $d_{JL} \times 10^3$ | | −14.381(23) | 52.55(18) |
| $h_{JL} \times 10^6$ | | 0.0571(39) | |
| $r_{67} \times 10^{-3}$ | | | −10.0538(28) |
| $r_{67J} \times 10^3$ | | | −12.327(76) |

$^a$ Estimated value to account for vibrational dependence of the parameter, see text Section 3.1.1. $^b$ Constrained to the values $q_7$, $q_{7J}$, $q_{7JJ}$, $q_6$ and $q_{6J}$ of (0,0,0,1) and (0,0,1,0), respectively.

**Table 3** Molecular constants (MHz) of HCCC$^{15}$N

| Parameter | (0,0,0,0) | (0,0,1,0) | (0,1,0,0) |
|---|---|---|---|
| $B_v$ | 4416.752 38(13) | 4425.787 96(56) | 4417.2421(17) |
| $D_v \times 10^3$ | 0.511 450(53) | 0.521 67(23) | 0.5075(36) |
| $H_v \times 10^9$ | 0.0381(63) | 0.111(28) | |
| $q_t$ | | 3.386 41(56) | 2.397 12(92) |
| $q_{tJ} \times 10^6$ | | −1.850(92) | |
| | (0,0,0,1) | (0,0,0,2) | (0,0,1,1) |
| $B_v$ | 4430.759 93(21) | 4444.761 99(34) | 4439.8879(53) |
| $D_v \times 10^3$ | 0.534 115(76) | 0.556 638(73) | 0.550(10) |
| $H_v \times 10^9$ | 0.0973(83) | | |
| $q_t$ | 6.207 808 1(13) | 6.232 639 3$^a$ | $^b$ |
| $q_{tJ} \times 10^6$ | −15.057 35(88) | −15.659 64$^a$ | $^b$ |
| $q_{tJJ} \times 10^{12}$ | 51.71(14) | 62.05$^a$ | $^b$ |
| $x_L \times 10^{-3}$ | | 21.8640(21) | 16.633(11) |
| $d_{JL} \times 10^3$ | | −10.945(86) | 48.0$^c$ |
| $r_{67} \times 10^{-3}$ | | | −11.502(25) |
| $r_{67J} \times 10^3$ | | | −9.92(68) |

$^a$ Estimated value to account for vibrational dependence of the parameter, see text Section 3.1.1. $^b$ Constrained to the values $q_7$, $q_{7J}$, $q_{7JJ}$, $q_6$ and $q_{6J}$ of (0,0,0,1) and (0,0,1,0), respectively. $^c$ Kept fixed in the analysis.

**Table 4** Molecular constants (MHz) of $H^{13}CCCN$

| Parameter | (0,0,0,0) | (0,0,0,1) | (0,0,0,2) | (0,0,1,0) |
|---|---|---|---|---|
| $B_v$ | 4408.441 738(79) | 4422.508 92(10) | 4436.570 399(81) | 4417.400 764(75) |
| $D_v \times 10^3$ | 0.510 294(38) | 0.533 037(42) | 0.556 563(27) | 0.519 831(32) |
| $H_v \times 10^9$ | 0.0453(47) | 0.0931(48) | 0.1481(29) | 0.0490(38) |
| $q_t$ | | 6.180 76(21) | 6.205 48$^a$ | 3.366 80(10) |
| $q_{tJ} \times 10^6$ | | −15.036(84) | −15.637$^a$ | −1.854(15) |
| $q_{tJJ} \times 10^{12}$ | | 53.8(97) | 64.6$^a$ | |
| $x_L \times 10^{-3}$ | | | 22.122 62(30) | |
| $d_{JL} \times 10^3$ | | | −10.159(21) | |
| $h_{JL} \times 10^6$ | | | 0.0817(38) | |
| | (0,1,0,0) | (0,0,0,3) | (0,0,1,1) | |
| $B_v$ | 4409.697 32(26) | 4450.601$^b$ | 4431.555 52(14) | |
| $D_v \times 10^3$ | 0.5115$^b$ | 0.5797$^b$ | 0.542 03(23) | |
| $H_v \times 10^9$ | | 0.21$^b$ | | |
| $q_t$ | 2.405 87(16) | 6.2283$^b$ | $^d$ | |
| $q_{tJ} \times 10^6$ | −1.3$^b$ | −15.64$^b$ | $^d$ | |
| $q_{tJJ} \times 10^9$ | | | $^d$ | |
| $x_L \times 10^{-3}$ | | 21.901$^b$ | 17.0267(28) | |
| $d_{JL} \times 10^3$ | | −10.88$^b$ | 49.44(15) | |
| $h_{JL} \times 10^6$ | | 0.04$^b$ | | |
| $r_{67} \times 10^{-3}$ | | | −11.5179(29) | |
| $r_{67J} \times 10^3$ | | | −12.712(63) | |
| $\Delta E_{(0,0,0,3)-(0,1,0,0)}$ | 2274(78) | | | |
| $F_0$ | 1119.12$^c$ | | | |
| $F_{0J} \times 10^3$ | −64.002$^c$ | | | |

[a] Estimated value to account for vibrational dependence of the parameter, see text Section 3.1.1. [b] Estimated value, see text Section 3.1.2. [c] Value taken from $HCC^{13}CN$ isotopomer, see text Section 3.1.2 and Table 1. [d] Constrained to the values $q_7$, $q_{7J}$, $q_{7JJ}$, $q_6$ and $q_{6J}$ of (0,0,0,1) and (0,0,1,0), respectively.

**Table 5** Molecular constants (MHz) of $HC^{13}C^{13}CN$

| Parameter | (0,0,0,0) | (0,0,0,1) | (0,0,1,0) |
|---|---|---|---|
| $B_v$ | 4510.323 982(85) | 4524.104 067(67) | 4519.112 31(12) |
| $D_v \times 10^3$ | 0.538 803(49) | 0.561 36(11) | 0.548 70(21) |
| $H_v \times 10^9$ | 0.0451(87) | | |
| $q_t$ | | 6.558 66(13) | 3.644 662(48) |
| $q_{tJ} \times 10^6$ | | −15.74(23) | −2.0$^a$ |
| | (0,1,0,0) | (0,0,0,2) | (0,0,1,1) |
| $B_v$ | 4511.8630(29) | 4537.888 89(11) | 4532.991 51(53) |
| $D_v \times 10^3$ | 0.5399(63) | 0.584 53(19) | 0.570 77(90) |
| $q_t$ | 2.501 13(62) | 6.584 89$^b$ | $^c$ |
| $q_J \times 10^6$ | | −16.37$^b$ | $^c$ |
| $x_L \times 10^{-3}$ | | 19.5707(16) | 16.1612(72) |
| $d_{JL} \times 10^3$ | | −17.048(18) | 61.89(56) |
| $r_{67} \times 10^{-3}$ | | | −10.6611(89) |
| $r_{67J} \times 10^3$ | | | −13.30(20) |

[a] Kept fixed in the analysis. [b] Estimated value to account for vibrational dependence of the parameter, see text Section 3.1.1. [c] Constrained to the values $q_7$, $q_{7J}$, $q_6$ and $q_{6J}$ of (0,0,0,1) and (0,0,1,0), respectively.

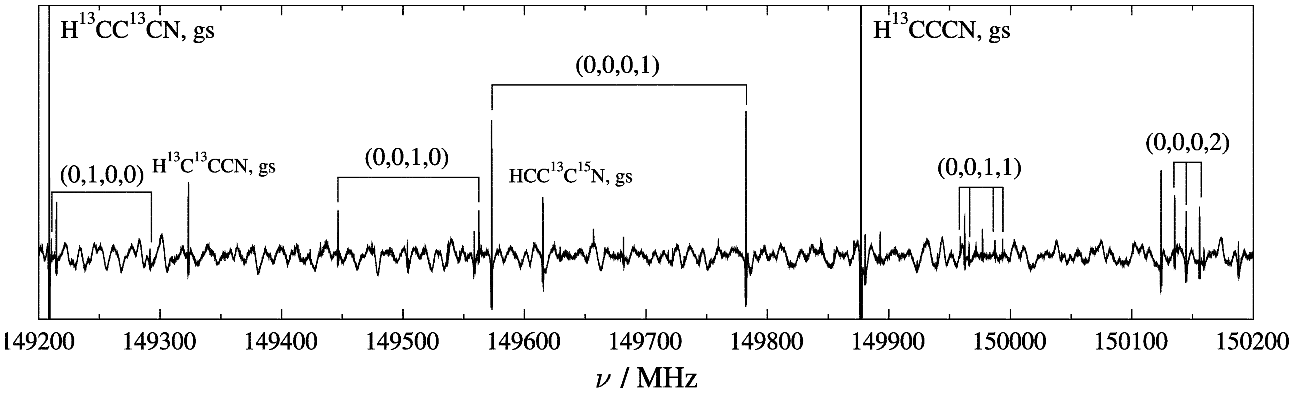

**Fig. 2** An example for the spectra recorded in the 2 mm range showing the $J = 17–16$ transitions of $H^{13}CC^{13}CN$, $H^{13}C^{13}CCN$, $HCC^{13}C^{15}N$ and $H^{13}CCCN$. For the sake of lucidity, only vibrational satellites of $H^{13}CC^{13}CN$ are indicated. The signal to noise is rather poor due to the low abundances of these isotopomers in the sample. Thus, vibrational satellites of $H^{13}C^{13}CCN$ and $HCC^{13}C^{15}N$ can hardly be discovered in this spectrum. An example for the (0,0,0,2) state of $HCC^{13}C^{15}N$ is given in Fig. 3.

**Table 6** Molecular constants (MHz) of $H^{13}CC^{13}CN$

| Parameter | (0,0,0,0) | (0,0,0,1) | (0,0,1,0) |
|---|---|---|---|
| $B_v$ | 4388.787 145(65) | 4402.590 069(86) | 4397.488 08(16) |
| $D_v \times 10^3$ | 0.507 611(36) | 0.529 14(14) | 0.516 36(25) |
| $H_v \times 10^9$ | 0.0396(62) | | |
| $q_t$ | | 6.167 40(17) | 3.408 016(66) |
| $q_{tJ} \times 10^6$ | | −15.12(27) | −2.0[a] |
| | (0,1,0,0) | (0,0,0,2) | (0,0,1,1) |
| $B_v$ | 4390.032 05(75) | 4416.390 25(18) | 4411.383 22(21) |
| $D_v \times 10^3$ | 0.5074(12) | 0.552 56(27) | 0.538 12(33) |
| $q_t$ | 2.385 99(27) | 6.192 07[b] | [c] |
| $q_{tJ} \times 10^6$ | | −15.72[b] | [c] |
| $x_L \times 10^{-3}$ | | 21.3518(44) | 17.2520(42) |
| $d_{JL} \times 10^3$ | | −12.654(34) | 58.85(23) |
| $r_{67} \times 10^{-3}$ | | | −12.7569(56) |
| $r_{67J} \times 10^3$ | | | −15.033(85) |

[a] Kept fixed in the analysis. [b] Estimated value to account for vibrational dependence of the parameter, see text Section 3.1.1. [c] Constrained to the values $q_7$, $q_{7J}$, $q_6$ and $q_{6J}$ of (0,0,0,1) and (0,0,1,0), respectively.

the energy differences found for the parent molecule HCCCN in two different fits[5] (133 089.26(47) *vs.* 4179.(120)/4559.(82) MHz respectively, 4.44 *vs.* 0.14/0.15 cm$^{-1}$) demonstrating a significant isotopic shift. The strength of the interaction for both isotopomers is similar, as revealed by the values obtained for the Fermi parameters (1119.12(26) *vs.* 1128.5(80)/1099.6(55) MHz). The centrifugal distortion corrections to $F_0$ agree less well (−64.002(82) *vs.* −35.3(63)/−40.7(52) kHz). This may be caused by the fact that (0,1,0,0) and (0,0,0,3) do not cross for the main isotopomer. Additionally, it may be a further manifestation of the weak Coriolis resonance between (0,0,0,3) and (0,0,1,1) which should be more pronounced in HCC$^{13}$CN than in the main isotopomer HCCCN because of the smaller energy difference. An inclusion of this resonance into the fit may affect some of the parameters to a non-negligible amount, in particular those of higher order.

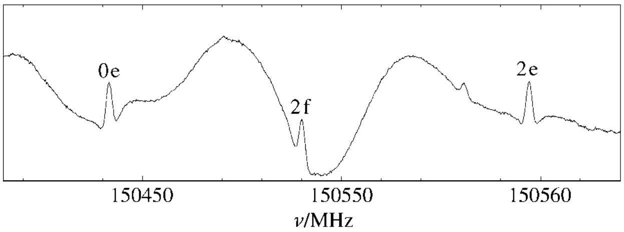

**Fig. 3** The three components of the $J = 17$–$16$ transition of $HCC^{13}C^{15}N$ in its (0,0,0,2) vibrational state around 150.55 GHz.

### 3.1.2. $HC^{13}CCN$, $H^{13}CCCN$, $HCCC^{15}N$.

Since the rotational constant $B$ of $HC^{13}CCN$ differs only slightly from that of $HCC^{13}CN$ (4529.8 *vs.* 4530.2 MHz), the spectra of the two molecules were recorded simultaneously in the 2 mm range. $H^{13}CCCN$ was investigated in natural abundance as well as using the $^{13}C$ enriched sample in the 2 mm range. In the submm range, $H^{13}CCCN$ was exclusively investigated using the $^{13}C$ enriched sample. Vibrational satellites for the (0,0,0,3) states were recorded for none of the three isotopomers. Thus, the (0,1,0,0) vibrational states of $HC^{13}CCN$ and $HCCC^{15}N$ were treated as isolated states. The effective constants obtained are shown in Tables 2 and 3. In contrast, this approach did not yield satisfactory results for $H^{13}CCCN$. In this case, the weighted rms (wrms) of the fit was found to be approximately 9. Therefore, another strategy was employed: Appropriate parameters for the resonant (0,0,0,3) state were estimated by scaling the corresponding values obtained for the main isotopomer HCCCN[5] and $HCC^{13}N$ (this work). As Fermi parameters, the corresponding values $F_0$ and $F_{0J}$ of the $HCC^{13}CN$ isotopomer were used. Except for $B_{(0,1,0,0)}$,

**Table 7** Molecular constants (MHz) of $H^{13}C^{13}CCN$

| Parameter | (0,0,0,0) | (0,0,0,1) | (0,0,1,0) |
|---|---|---|---|
| $B_v$ | 4392.156 50(36) | 4405.813 10(14) | 4400.943 38(42) |
| $D_v \times 10^3$ | 0.507 02(57) | 0.529 44(23) | 0.517 13(66) |
| $q_t$ | | 6.225 91(29) | 3.384 53(18) |
| $q_{tJ} \times 10^6$ | | −15.44(46) | −2.0[a] |

[a] Kept fixed in the analysis.

**Table 8** Molecular constants (MHz) of $HCC^{13}C^{15}N$

| Parameter | (0,0,0,0) | (0,0,0,1) | (0,0,0,2) | (0,0,1,0) |
|---|---|---|---|---|
| $B_v$ | 4400.741 388(46) | 4414.498 40(18) | 4 428.253 12(49) | 4409.513 90(53) |
| $D_v \times 10^3$ | 0.509 318(23) | 0.531 60(29) | 0.553 47(69) | 0.517 18(82) |
| $H_v \times 10^9$ | 0.0335(38) | | | |
| $q_t$ | | 6.207 06(37) | 6.231 88[a] | 3.433 36(20) |
| $q_{tJ} \times 10^6$ | | −14.97(57) | −15.57[a] | −2.0[b] |
| $x_L \times 10^{-3}$ | | | 21.0364(95) | |
| $d_{JL} \times 10^3$ | | | −13.759(91) | |

[a] Estimated value to account for vibrational dependence of the parameter, see text Section 3.1.1. [b] Kept fixed in the analysis.

$q_{(0,1,0,0)}$ and the energy difference $\Delta E$ the parameters were kept fixed in the analysis (see Table 4). The wrms was found to decrease to 0.33 and the value obtained for the energy difference $\Delta E$ is similar to the corresponding value found for the parent molecule HCCCN (2274.(78) *vs.* 4179.(120)/4559.(82) MHz). Since only transitions for the (0,1,0,0) vibrational state could be used in the fit the results obtained should be viewed with some caution.

HCCC$^{15}$N was exclusively investigated in natural abundance. For the (0,0,0,1) vibrational state the direct *l*-type transitions of ref. 14 were included in the fit to obtain highly determined values for the *l*-type doubling constant $q$ and its centrifugal distortion corrections. For the relatively weak (0,1,0,0) state only the $J = 14$–13, $J = 15$–14 and $J = 16$–15 vibrational satellites could be detected. The respective apparent line positions of the 1f components were found to be heavily influenced by the much stronger $(0,0,0,1)^{1e}$ components of H$^{13}$CCCN as revealed by the larger uncertainties attributed to the respective transition frequencies (see Table S3).† Nevertheless, the value obtained for the *l*-type doubling constant $q_5$ is in reasonable agreement with the values obtained from quantum chemical calculations.[23,24]

The molecular constants for all monosubstituted isotopomers derived from the inclusion of all now available data are shown in Tables 1–4.

### 3.2. Doubly substituted isotopomers

In addition to the investigation of monosubstituted isotopomers, the doubly substituted isotopomers HC$^{13}$C$^{13}$CN, H$^{13}$CC$^{13}$CN, H$^{13}$C$^{13}$CCN and HCC$^{13}$C$^{15}$N, respectively, could be detected for the first time. Furthermore, these isotopomers could be observed not only in the ground but even in the (0,0,0,1) and (0,0,1,0) vibrationally excited states in all instances. For some of these isotopomers also the (0,0,0,2), (0,0,1,1) and (0,1,0,0) vibrational states could be observed (see Tables S5–S8† and Tables 5–8 for details). Vibrational satellites were recorded in the 2 mm range exclusively. Selected transitions of doubly substituted isotopomers in their ground vibrational states were recorded up to 532 GHz. Figs. 2 and 3 show examples for spectra obtained in the 2 mm range.

The molecular constants derived for the doubly substituted isotopomers are shown in Tables 5–8.

## 4. Conclusions

The pure rotational spectra of eight HC$_3$N isotopomers in their ground and a variety of vibrationally excited states have been measured in selected frequency regions from 118 to 625 GHz. The Fermi resonance system (0,1,0,0)/(0,0,0,3) has been analyzed succesfully for HCC$^{13}$CN and H$^{13}$CCCN. Moreover, the doubly substituted isotopomers HC$^{13}$C$^{13}$CN, H$^{13}$CC$^{13}$CN, H$^{13}$C$^{13}$CCN and HCC$^{13}$C$^{15}$N have been investigated for the first time. All data have been fitted within experimental accuracy. For the monosubstituted isotopomers, the new data permits accurate frequency predictions far into the submm range and should therefore be of importance for interpreting astronomical data. Due to improved instrumentation the frequency regime accessible to radio telescopes has been greatly expanded in the recent past and will still be enlarged considerably toward higher frequencies in the future with the advent of SOFIA (Stratospheric Observatory For Infrared Astronomy) in 2002 and the Herschel Space Observatory (formerly known as FIRST) in 2007.

## 5. Cologne database for molecular spectroscopy, CDMS

The Cologne database for molecular spectroscopy (CDMS) contains spectroscopic data on molecules of astrophysical as well as atmospherical importance and can be found online *via*: http://www.ph1.uni-koeln.de/vorhersagen/ or alternatively *via* the shortcut: http://www.cdms.de.

All data related to the results presented here (line lists, fit files) can be found online in the CDMS through: http://www.ph1.uni-koeln.de/vorhersagen/daten/.

The fits give experimental lines, spectroscopic constants and their uncertainties. For predictions on the states of all isotopomers presented here, for any additional information on the catalog and for further catalog entries visit: http://www.ph1.uni-koeln.de/vorhersagen/catalog.

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