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A CONCISE NEW LOOK AT THE *l*-TYPE SPECTRUM OF $H^{12}C^{14}N$

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ABSTRACT

In response to our recent astrophysical discovery of highly excited circumstellar $H^{12}C^{14}N$ gas via direct *l*-type transitions, we have conducted comprehensive and precise laboratory measurements of those transitions ($v_2 = 1$, $\Delta J = 0$). The newly measured transitions cover the *J*-values from $15 \leq J \leq 35$ and span the frequency range from 53 to 279 GHz. In addition, these new laboratory data are complemented by precision recordings of three medium $\Delta J = 1$ (*R*-branch) transitions with $J = 19$, 20, and 21 near 2 THz in the ground vibrational and the $v_2 = 1$ bending state. Third, we supply the $v_2 = 1$ vibrational satellites between 440 and 980 GHz of $5 \leq J_u \leq 11$. The latter measurements were carried out in sub-Doppler resolution. All these new data are highly relevant to astrophysics.

Subject headings: methods: laboratory — molecular data — techniques: spectroscopic

1. INTRODUCTION

In recent years, molecular discoveries in astrophysics have set the pace in regulating the speed of laboratory spectroscopy in certain specific areas. In this context, $H^{12}C^{14}N$ is a well-studied molecule since it has been the matter of a wide range of laboratory spectroscopic studies from the microwave region to the infrared (e.g., Maki 1974; Maki et al. 2000; Ahrens et al. 2002). However, our recent astronomical detection of direct *l*-type transitions[1] of $H^{12}C^{14}N$ in its $v_2 = 1$ vibrational state in the proto–planetary nebula CRL 618 (Thorwirth et al. 2003) asks for a quick reply from laboratory spectroscopy. In this Letter, we supply missing transition frequencies of direct *l*-type transitions up to $J = 35$. Moreover, we have complemented earlier measurements on HCN by observing the *l*-type doubling *R*-branch ($\Delta J = 1$) transitions of HCN in its $v_2 = 1$ vibrationally excited state: three consecutive Doppler-resolved *R*-branch ($\Delta J = 1$) transitions of HCN have been measured close to 2 THz in the shape of the $J = 20$–19, 21–20, and 22–21 transitions. Finally, *R*-branch transitions have been measured from 440 to 980 GHz employing the Lamb-dip technique.

2. EXPERIMENTAL

For the spectroscopic investigations, three different spectrometers were employed: the "conventional" millimeter-wave range (<180 GHz) was covered by a commercial spectrometer purchased from Analytik & Messtechnik GmbH, Chemnitz. A detailed description of the instrument was given by Winnewisser, Lichau, & Wolf (2000). At shorter millimeter waves ($\lambda < 2$ mm) and the submillimeter-wave range (180–980 GHz), the Cologne terahertz spectrometer was used (Winnewisser et al. 1994; Winnewisser 1995), while spectra close to 2 THz were recorded employing the Cologne sideband spectrometer for terahertz applications (COSSTA; Gendriesch et al. 2000). Schottky diodes as well as liquid He cooled InSb bolometers served as detectors in conjunction with 1–4 m free-space absorption cells. The measurements of direct *l*-type transitions with $J \geq 28$ and the Lamb-dip measurements were carried out with a 4 m cell heated over its entire length to a temperature of approximately 350 K.

[1] See, e.g., Thorwirth et al. (2003) for theoretical details on direct *l*-type transitions.

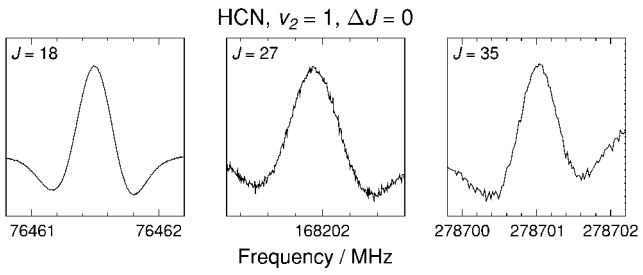

FIG. 1.—Example spectra of direct *l*-type ($\Delta J = 0$) transitions with $J = 18$, 27, and 35.

3. ANALYSIS AND DISCUSSION

Theoretical details concerning the appropriate treatment of the data can be found in Reinartz & Dymanus (1974) and Thanh & Rossi (1993). It may be noted that the denotation of the spectroscopic constants may differ occasionally. We employed a Hamiltonian of the form

$$\mathcal{H} = \mathcal{H}_{\rm rot} + \mathcal{H}_{\rm doub} + \mathcal{H}_{\rm hfs} \quad (1)$$

accounting for the different contributions of rotation, *l*-type doubling, and hyperfine structure due to the ^{14}N nucleus.

In the present investigation, a total of 21 direct *l*-type tran-

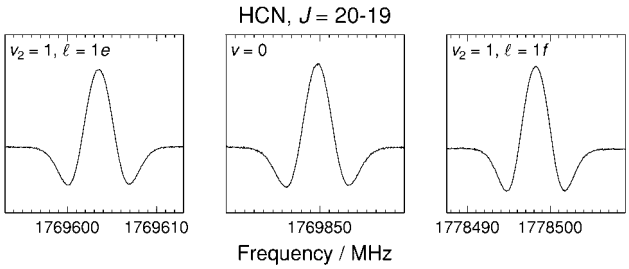

FIG. 2.—Example spectra taken at 1.8 THz showing the $J = 20$–19 transition of HCN in the ground vibrational state along with the two vibrational satellites corresponding to $v_2 = 1$.

TABLE 1

DIRECT l-TYPE ($\Delta J = 0$) TRANSITIONS OF HCN IN ITS $v_2 = 1$ STATE MEASURED IN THE PRESENT INVESTIGATION AND RESIDUALS $O - C$

J	Frequency (MHz)	$O - C$ (kHz)
15	53721.715 (10)	−10
16	60861.651 (10)	2
17	68441.925 (10)	0
18	76461.493 (10)	0
19	84919.252 (10)	19
20	93813.982 (15)	15
21	103144.470 (20)	10
22	112909.422 (20)	6
23	123107.475 (20)	−12
24	133737.264 (20)	0
25	144797.280 (20)	−6
26	156286.022 (20)	−14
27	168201.936 (20)	−7
28	180543.381 (10)	−1
29	193308.672 (10)	−3
30	206496.098 (10)	4
31	220103.857 (20)	−2
32	234130.151 (30)	13
33	248573.053 (20)	0
34	263430.665 (30)	−9
35	278701.031 (30)	5

sitions have been observed from $15 \leq J \leq 35$, which are presented in Table 1. Three example spectra in the shape of the $J = 18$, 27, and 35 transitions are shown in Figure 1. Since direct l-type transitions obey the selection rule $\Delta J = 0$ (Q-branch), they do not contain any information on the rotational constant B, but they allow the evaluation of the l-type doubling constant q and its centrifugal distortion corrections with high accuracy and hyperfine structure constants for the $v_2 = 1$ state at low values of J.

Doppler-limited spectra of $\Delta J = 1$ transitions (*vibrational satellites*)[2] have been obtained employing the COSSTA, covering the quantum numbers $20 \leq J_u \leq 22$. The corresponding transition frequencies are given in Table 2. In addition, the $J = 20$–19 ground-state transition has been newly measured and is quoted here for the sake of completeness. An example spectrum showing the $J = 20$–19 transition is shown in Figure 2.

Additional vibrational satellites have been recorded in the frequency range from 440 to 980 GHz ($5 \leq J_u \leq 11$) employing the Lamb-dip technique resulting in sub-Doppler resolution (see Table 3). An example spectrum is shown in Figure 3. This technique enabled the resolution of nuclear quadrupole hyperfine structure due to the ^{14}N nucleus even at relatively high values of J. Details on this experimental technique including information on the occurrence of crossover dips C in sub-Doppler spectra have been recently summarized by Ahrens et al. (2002), in which the ground-state spectra were measured in the sub-Doppler mode.

The analysis has been performed using Pickett's program SPFIT (Pickett 1991), fitting the $v_2 = 0$, 1 states simultaneously under consideration of the pure rotational data as well

[2] "Vibrational satellites" denote pure rotational transitions of any vibrationally excited molecule. Each vibrationally excited state causes an individual set of vibrational satellites.

TABLE 2

TRANSITION FREQUENCIES MEASURED CLOSE TO 2 THz AND RESIDUALS $O - C$

$J' \leftarrow J''$	v[a]	Frequency (MHz)	$O - C$ (kHz)
20 ← 19	1	1769603.495 (30)	24
20 ← 19	0	1769849.756 (20)	20
20 ← 19	1	1778498.217 (20)	12
21 ← 20	1	1857781.275 (20)	−2
21 ← 20	1	1867111.729 (50)	−41
22 ← 21	1	1945914.855 (20)	−20
22 ← 21	1	1955679.825 (20)	−7

[a] 0 and 1 denote the $v_2 = 0$ and 1 states, respectively.

TABLE 3

SUB-DOPPLER MEASUREMENTS OF VIBRATIONAL SATELLITES OF HCN IN ITS $v_2 = 1$ STATE AND RESIDUALS $O - C$[a]

J'	F'		J''	F''	l	Frequency (MHz)	$O - C$ (kHz)
5	5	←	4	5	1e	443058.282 (5)	−3
5	5; 4	←	4	4; 3		443059.671 (15)	−10
5	6	←	4	5		443059.775 (15)	2
5	$C_{5,\,4;\,4,\,4}$	←	4	$C_{4,\,4;\,4,\,3}$		443060.505 (3)	−2
5	4	←	4	4		443061.327 (5)	−3
6	6	←	5	6	1e	531646.944 (5)	4
6	$C_{7,\,6;\,6,\,6}$	←	5	$C_{6,\,6;\,6,\,5}$		531647.700 (3)	−2
6	6; 5	←	5	5; 4		531648.440 (10)	6
6	7	←	5	6		531648.510 (15)	11
6	$C_{6,\,5;\,5,\,5}$	←	5	$C_{5,\,5;\,5,\,4}$		531649.276 (3)	3
6	5	←	5	5		531650.113 (5)	2
6	6	←	5	6	1f	534338.230 (5)	5
6	$C_{7,\,6;\,6,\,6}$	←	5	$C_{6,\,6;\,6,\,5}$		534339.061 (3)	4
6		←	5			534339.885 (3)	1
6	$C_{6,\,5;\,5,\,5}$	←	5	$C_{5,\,5;\,5,\,4}$		534340.773 (3)	−6
6	5	←	5	5		534341.700 (5)	0
7	7	←	6	7	1e	620222.968 (5)	1
7	$C_{8,\,7;\,7,\,7}$	←	6	$C_{7,\,7;\,7,\,6}$		620223.762 (3)	3
7		←	6			620224.545 (3)	−1
7	$C_{7,\,6;\,6,\,6}$	←	6	$C_{6,\,6;\,6,\,5}$		620225.369 (3)	0
7	$C_{8,\,7;\,7,\,7}$	←	6	$C_{7,\,7;\,7,\,6}$	1f	623362.721 (3)	5
7		←	6			623363.573 (3)	0
7	$C_{7,\,6;\,6,\,6}$	←	6	$C_{6,\,6;\,6,\,5}$		623364.479 (3)	0
8	8	←	7	8	1e	708784.236 (5)	−10
8	$C_{9,\,8;\,8,\,8}$	←	7	$C_{8,\,8;\,8,\,7}$		708785.060 (3)	0
8		←	7			708785.858 (10)	−9
8	$C_{8,\,7;\,7,\,7}$	←	7	$C_{7,\,7;\,7,\,6}$		708786.693 (3)	−1
8	7	←	7	7		708787.533 (5)	−2
9		←	8		1e	797330.319 (3)	2
9		←	8		1f	801363.150 (3)	−4
10		←	9		1e	885855.790 (3)	2
10		←	9		1f	890334.706 (3)	2
11		←	10		1e	974360.172 (3)	−1
11		←	10		1f	979284.531 (3)	−3

[a] If two values are given for F' and F'' separated by a semicolon, this indicates an overlap of the corresponding two hyperfine components (e.g. 7; 6 ← 6; 5 means 7 ← 6 and 6 ← 5). If no value is given, this indicates the overlap of all three $\Delta F = 1$ components. Each crossover line C is an overlap of two crossover transitions. The subscripts denote the involved F quantum numbers, and as in the former case semicolons separate the quantum numbers belonging to the individual transitions.

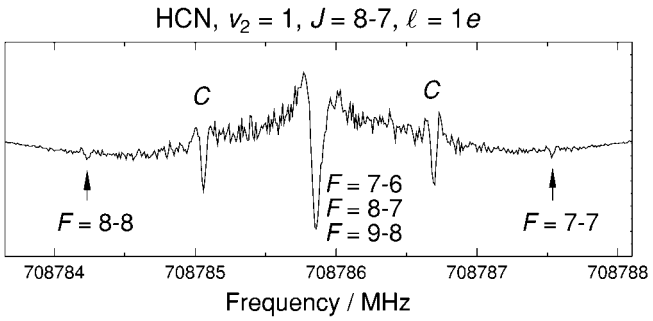

FIG. 3.—Example sub-Doppler spectrum highlighting the hyperfine structure of a $J = 8$–7 vibrational satellite. In addition to the $\Delta F = 0$ and $\Delta F = 1$ components, two crossover dips C can be seen (see Table 3 for details of assignment and Ahrens et al. 2002 for corresponding theoretical details).

TABLE 4

MOLECULAR PARAMETERS OF HCN AS DETERMINED IN THE PRESENT INVESTIGATION AND IN COMPARSION TO PREVIOUS INVESTIGATIONS

	PRESENT INVESTIGATION		PREVIOUS INVESTIGATIONS	
PARAMETER	$v_2 = 0$ (MHz)	$v_2 = 1$ (MHz)	$v_2 = 0$ (MHz)	$v_2 = 1$ (MHz)
B	44 315.975 60 (12)	44 422.426 83 (13)	44 315.974 97 (16)[a]	44 422.427 63 (97)[b]
$D \times 10^3$	87.216 80 (73)	89.230 42 (83)	87.216 4 (17)[a]	89.262 0 (48)[b]
$H \times 10^9$	85.85 (95)	104.58 (102)	87.0 (24)[a]	117.3 (20)[b]
q_2		224.476 804 (14)		224.476 723 (51)[b]
$q_{2J} \times 10^3$		−2.661 674 (90)		−2.660 6 (54)[b]
$q_{2JJ} \times 10^9$		43.89 (15)		40.83 (36)[b]
$q_{2JJJ} \times 10^{12}$		−0.740 (76)		…
eQq	−4.709 6 (15)	−4.812 09 (62)	−4.707 83 (6)[c]	−4.809 2 (11)[d]
$eQq_J \times 10^3$	0.212 (61)[e]			…
eQq_η		0.393 10 (81)		0.392 2 (16)[d]
$eQq_{\eta J} \times 10^3$		0.289 (63)		…
$C_\parallel - C_\perp \times 10^3$		4.16 (90)		…
$C_\perp \times 10^3$	10.67 (33)	10.09 (45)	10.13 (2)[c]	12.2 (2)[d]
$C_{\perp J} \times 10^6$	−10.1 (61)[e]		−14.3 (86)[a]	…
$C_- \times 10^3$		−0.33 (15)		…
ΔE	21389032.61 (21)		21389032.94 (27)[b]	
wrms[f]	0.88			

[a] Taken from Ahrens et al. 2002.
[b] Taken from Maki et al. 2000.
[c] Taken from Ebenstein & Muenter 1984.
[d] Taken from Radford & Kurtz 1970.
[e] Common constant for both states.
[f] Weighted rms of the least-squares fit (dimensionless).

as rotation-vibration data available in the literature (Maki 1974; Fliege et al. 1984; Maiwald 2000; Maki et al. 2000; Ahrens et al. 2002). The data were weighted inversely proportional to the square of the experimental uncertainties. It has to be noted that only field-free data can be treated with the program, so the electric resonance data of Ebenstein & Muenter (1984) could not be taken into account. The complete set of molecular constants is shown in Table 4. The major impact of the new data is focused on the $v_2 = 1$ state. There is an overall refinement of the rotational constants of the $v_2 = 1$ state in comparison to previous investigations. Moreover, several constants have been determined for the first time, such as the *l*-type doubling distortional correction q_{2JJJ} and the nuclear spin-rotation interaction constants $C_\parallel$ and C_-. The rest of the constants confirm the results reported in previous investigations, since these data also represent the basis of the present fit.

As revealed by the weighted rms of 0.88, the experimental transition frequencies have been reproduced within their uncertainties. The present data set allows for prediction of accurate transition frequencies far beyond 2 THz.

4. COLOGNE DATABASE FOR MOLECULAR SPECTROSCOPY

All data related to the results presented here (line list, fit file, etc.) as well as frequency predictions based on the current parameter set can be found on-line in the Cologne Database for Molecular Spectroscopy (Müller et al. 2001).[3]

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[3] See http://www.cdms.de.

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