l-Type Doublet Transitions of the Rare Stable Isotopic Species of Hydrogen Cyanide, HCN

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l-type doublet transitions for HCN molecules in the first excited bending state 01^10 have been measured for the isotopic species $H^{13}C^{14}N$, $H^{12}C^{15}N$, $H^{13}C^{15}N$, $D^{13}C^{14}N$, $D^{12}C^{15}N$ and $D^{13}C^{15}N$. The measurements improve and complete the set of available coupling constants of the vibration-rotation interaction in this bending mode. All known l-type coupling constants are collected and compared with those obtained from the l-type splitting of the rotational lines and those obtained from ab-initio calculation of the energy hypersurface.

I. Introduction

Hydrogen cyanide, HCN, is a simple triatomic linear molecule and its vibration-rotation spectrum has consequently been studied extensively in the infrared region [1–4] and in the microwave region [4, 5, 6] for the main isotopic species $H^{12}C^{14}N$ and $D^{12}C^{14}N$. Recently the main isotopic species $H^{12}C^{14}N$ has been studied in highly excited vibrational states by millimeter wave spectroscopy in active laser plasmas [7]. For the species which contain ^{13}C and ^{15}N, however, the vibration-rotation interaction constants have been determined only by measurements of the l-type doublet transitions in the frequency range between 6.5 and 26.0 GHz, using the isotopic species in their natural abundances [8]. These interactions have also been investigated for some isotopic species containing tritium from the l-type splitting of the rotational lines by millimeter wave measurements [9].

In this paper direct l-type doublet transitions of isotopically enriched samples, which have been studied in the microwave region from 8 to 53 GHz, are reported for the first excited bending state. Hereby the microwave spectra of the doubly enriched isotopic species $H^{13}C^{15}N$ and $D^{13}C^{15}N$ have been obtained for the first time, whereas transitions of the other isotopic species have been remeasured with higher accuracy in a wider frequency range. Unpublished results of the l-type splitting of some rotational lines, which were measured in the course of the determination of the substitution structure of hydrogen cyanide and hydrogen isocyanide [10], are presented for the isotopic species $H^{12}C^{15}N$, $H^{13}C^{15}N$, $D^{12}C^{15}N$ and $D^{13}C^{15}N$. The resulting l-type doubling parameters are collected and compared with those constants taken from the literature and with those obtained by ab-initio calculation of the energy hypersurface [11].

The investigation of the microwave and millimeter wave spectrum of the radioactive isotopic species $H^{14}C^{14}N$ and $D^{14}C^{14}N$ is planned in order to complete this work. These measurements should be of considerable astrophysical interest to provide data to possibly detect the unstable carbon isotopic species in the interstellar matter. In general the isotopic species of hydrogen cyanide are useful for the determination of the relative isotopic abundances of the elements carbon, nitrogen and hydrogen in the interstellar medium.

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II. Experimental Procedures

The hydrogen cyanide samples were prepared by liberating this weak acid by means of phosphoric acid from the solid potassium cyanide salt and in the deuterated cases by means of deuterated sulfuric acid. The following isotopically enriched potassium cyanides were used: $K^{12}C^{15}N$ (95.2 atom% ^{15}N) and $K^{13}C^{15}N$ (90.5 atom% ^{13}C and 95 atom% ^{15}N) available from B.O.C. Ltd. London and $K^{13}C^{14}N$ (90 atom% ^{13}C) available from Merck, Sharp and Dohme Canada Ltd.

The microwave measurements were performed in the frequency region from 8 GHz to 53 GHz using a Hewlett-Packard spectrometer, model 8460 MRR. Four different backward wave oscillators were used to generate the microwave power in the X, P, K and R-bands, whereas the frequency region above 40 GHz was covered by doubling the frequency of the K-band backward wave oscillator radiation. Sufficient power for spectroscopic purposes could

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Table 1. Observed and calculated line position of l-type doublet transitions arising from the $v_2 = 1$ bending state of isotopically substituted HCN molecules.

J	$H^{13}C^{14}N$			$H^{12}C^{15}N$			$H^{13}C^{15}N$		
	ν_{obs} [MHz]	ν_{cal} [MHz]	$\nu_{obs} - \nu_{cal}$ [kHz]	ν_{obs} [MHz]	ν_{cal} [MHz]	$\nu_{obs} - \nu_{cal}$ [kHz]	ν_{obs} [MHz]	ν_{cal} [MHz]	$\nu_{obs} - \nu_{cal}$ [kHz]
1	—	429.666	—	—	423.878	—	—	404.702	—
2	—	1 288.939	—	—	1 271.576	—	—	1 214.054	—
3	—	2 577.703	—	—	2 542.978	—	—	2 427.949	—
4	—	4 295.781	—	—	4 237.907	—	—	4 046.227	—
5	—	6 442.842	—	—	6 356.133	—	—	6 068.676	—
6	9 018.894[a]	9 018.893	1	8 897.365[a]	8 897.362	3	8 495.028	8 495.031	−3
7	12 023.283[a]	12 023.285	−2	11 861.244[a]	11 861.247	−3	11 324.970	11 324.974	−4
8	15 455.706[a]	15 455.709	−3	15 247.377[a]	15 247.382	−5	14 558.132	14 558.134	−2
9	19 315.698[a]	19 315.702	−4	19 055.303[a]	19 055.303	0	18 194.086	18 194.090	−4
10	23 602.738[a]	23 602.741	−3	23 284.485[a]	23 284.488	−3	22 232.373	22 232.367	6
11	28 316.261	28 316.246	15	27 934.377	27 934.362	15	26 672.436	26 672.438	−2
12	33 455.590	33 455.581	9	33 004.297	33 004.290	7	31 513.734	31 513.727	7
13	39 020.046	39 020.054	−8	38 493.585	38 493.583	2	36 755.622	36 755.606	16
14	45 008.909	45 008.915	−6	44 401.485	44 401.496	−11	42 397.360	42 397.396	−36
15	51 421.370	51 421.361	9	50 727.242	50 727.228	14	48 483.382	48 438.368	14
16	—	58 256.531	—	—	57 469.926	—	—	54 877.745	—
17	—	65 513.510	—	—	64 628.681	—	—	61 714.701	—
18	—	73 191.331	—	—	72 202.531	—	—	68 948.359	—
19	—	81 288.969	—	—	80 190.463	—	—	76 577.797	—
20	—	89 805.349	—	—	88 591.409	—	—	84 602.046	—
Standard deviation of the fit:									
	8.67 kHz			9.52 kHz			16.27 kHz		

[a] These lines have also been reported with less accuracy in Reference [8].

Table 2. Observed and calculated line positions of l-type doublet transitions arising from the $v_2 = 1$ bending state of isotopically substituted DCN molecules.

J	$D^{13}C^{14}N$			$D^{12}C^{15}N$			$D^{13}C^{15}N$		
	ν_{obs} [MHz]	ν_{cal} [MHz]	$\nu_{obs} - \nu_{cal}$ [kHz]	ν_{obs} [MHz]	ν_{cal} [MHz]	$\nu_{obs} - \nu_{cal}$ [kHz]	ν_{obs} [MHz]	ν_{cal} [MHz]	$\nu_{obs} - \nu_{cal}$ [kHz]
1	—	364.580	—	—	352.153	—	—	344.083	—
2	—	1 093.690	—	—	1 056.412	—	—	1 032.205	—
3	—	2 187.230	—	—	2 112.679	—	—	2 064.273	—
4	—	3 645.052	—	—	3 520.811	—	—	3 440.152	—
5	—	5 466.956	—	—	5 280.614	—	—	5 159.659	—
6	—	7 652.693	—	—	7 391.848	—	—	7 222.569	—
7	10 201.950[a]	10 201.967	−17	9 854.234[a]	9 854.225	9	9 628.610	9 628.609	1
8	—	13 114.429	—	12 667.417[a]	12 667.408	9	12 377.461	12 377.463	−2
9	16 389.686[a]	16 389.683	3	15 831.013[a]	15 831.012	1	15 468.768	15 468.769	−1
10	20 027.278[a]	20 027.284	−6	19 344.603[a]	19 344.606	−3	18 902.123	18 902.122	1
11	24 026.769[a]	24 026.737	32	23 207.706[a]	23 207.711	−5	22 677.071	22 677.072	−1
12	28 387.495	28 387.500	−5	27 419.790	27 419.799	−9	26 793.131	26 793.125	6
13	33 108.973	33 108.981	−8	31 980.287	31 980.297	−10	31 249.744	31 249.744	0
14	38 190.537	38 190.540	−3	36 888.584	36 888.584	0	36 046.361	36 046.350	11
15	43 631.491	43 631.492	−1	42 144.033	42 143.992	41	41 182.301	41 182.319	−18
16	49 431.108	49 431.101	7	47 745.792	47 745.807	−15	46 657.000	46 656.987	13
17	—	55 588.585	—	—	53 693.267	—	52 469.648	52 469.646	2
18	—	62 103.116	—	—	59 985.567	—	—	58 619.550	—
19	—	68 973.819	—	—	66 621.853	—	—	65 105.907	—
20	—	76 199.772	—	—	73 601.227	—	—	71 927.891	—
Standard deviation of the fit:									
	15.77 kHz			18.07 kHz			9.16 kHz		

[a] The lines have also been reported with less accuracy in Reference [8].

Table 3. l-type coupling constants q_i of the spectroscopically known isotopic species of hydrogen cyanide in the (01^10) state.

Isotopic species	From the direct l-type-doublet transitions			From the l-type splitting of the rotational lines	
	q_0 [MHz]	q_1 [kHz]	q_2 [Hz]	q_0 [MHz]	q_1 [kHz]
$H^{12}C^{14}N$	224.4766 ± 0.0004[a]	2.658 ± 0.003[a]	0.035 ± 0.005[a]	224.462 ± 0.017[b]	—
$H^{13}C^{14}N$	214.8378 ± 0.0002[c]	2.435 ± 0.002[c]	0.0418 ± 0.0067[c]	—	—
$H^{12}C^{15}N$	211.9440 ± 0.0002[c]	2.431 ± 0.002[c]	0.0511 ± 0.0073[c]	211.925[d,e]	—
$H^{13}C^{15}N$	202.3556 ± 0.0003[c]	2.216 ± 0.004[c]	0.0495 ± 0.0125[c]	202.335[d,e]	—
$D^{12}C^{14}N$	186.1916 ± 0.0005[a]	2.207 ± 0.003[a]	0.048 ± 0.005[a]	186.160[e,f]	—
$D^{13}C^{14}N$	182.2941 ± 0.0003[c]	2.075 ± 0.004[c]	0.0303 ± 0.0093[c]	—	—
$D^{12}C^{15}N$	176.0807 ± 0.0003[c]	2.008 ± 0.004[c]	0.0211 ± 0.0098[c]	176.075[d]	—
$D^{13}C^{15}N$	172.0455 ± 0.0001[c]	1.896 ± 0.001[c]	0.0429 ± 0.0033[c]	172.054[d]	—
$T^{12}C^{14}N$	—	—	—	150.822 ± 0.004[g]	1.91 ± 0.07[g]
$T^{13}C^{14}N$	—	—	—	149.749 ± 0.014[g]	1.41 ± 0.19[g]
$T^{12}C^{15}N$	—	—	—	142.688 ± 0.015[g]	1.98 ± 0.28[g]

[a] Reference [4].
[b] Calculated from Reference [7].
[c] Present work.
[d] Reference [17].
[e] Effective coupling constant of the vibration and rotation.
[f] From the computed linecentre, References [5] and [6].
[g] Corrected values of Reference [9].

be obtained over the frequency region from 40 GHz to 53 GHz. All measurements were performed in a two-meter X-band Stark cell at room temperature and with sample pressures of about 10 millitorr (1.3 Pa). The applied Stark voltages were chosen as high as possible in order to modulate the absorption lines as fully as possible. In the case of the deuterated species, however, the Stark effect electric field strengths were reduced in order to prevent a glow discharge in the absorption cell, since the sample pressures had to be increased because of the moderate degree of deuteration which could be maintained in the absorption cell. Therefore, most lines were measured with an electric field strength of the Stark field between 3000 and 3200 V/cm.

III. Theoretical Considerations

Since hydrogen cyanide is a triatomic linear molecule, there are three modes of vibration, of which the bending mode is doubly degenerate. This degeneracy is lifted due to the Coriolis coupling between vibration and end-over-end rotation. The quantum number l, which describes the internal angular momentum, is restricted by the vibrational quantum number v to $l = v, v-2, \ldots, -v$ and by the total angular momentum J to $J \geqq |l|$. For the first excited bending mode ($v=1$, $|l|=1$) the two eigenstates with $|l|=1$ are characterized by their parity for even J: $l = 1^e$ for $(+)(-1)^J$ parity and $l = 1^f$ for $(-)(-1)^J$ parity [12]. The splitting of the rotational term values is given in frequency units by

$$\Delta E = q\,J(J+1)\,. \tag{1}$$

The coupling constant q can be represented by

$$q = 2\frac{B_e^2}{\omega}\left\{1 + 4\sum_i \xi_i^2 \frac{\omega^2}{\omega_i^2 - \omega^2}\right\} \tag{2}$$

with

ω = frequency of the degenerate normal mode,
ω_i = frequency of the normal modes except ω,
ξ_i = Coriolis coupling constant,
B_e = equilibrium rotational constant.

According to the selection rules $\Delta J = \pm 1$ and $\Delta J = 0$ two different kinds of transitions are observable:

1) l-type splitting of the rotational lines

$J, l = J, 1^e \rightarrow J+1, 1^e$ and
$J, l = J, 1^f \rightarrow J+1, 1^f$.

2) Direct l-type doublet transitions

$J, l = J, 1^e \rightarrow J, 1^f$.

In order to fit the observed data for HCN it is necessary to consider higher order terms in the coupling constants. In most cases it is sufficient to truncate the series after the third term, so that we take [13, 14]

$$q = q_0 - q_1\,J(J+1) + q_2\,J^2(J+1)^2\,. \tag{3}$$

Table 4. Observed rotational l-type doubling transitions of the $(01^10)_{c,d}$ states of isotopically substituted HCN molecules[a].

Isotopic species	State	Rotational transitions in MHz $J = 2 \leftarrow 1$	$J = 3 \leftarrow 2$
$H^{12}C^{15}N$	$(01^10)_e$	172 093.067	
	$(01^10)_f$	172 940.765	
$H^{13}C^{15}N$	$(01^10)_e$	167 411.165	
	$(01^10)_f$	168 220.503	
$D^{12}C^{15}N$	$(01^10)_e$	140 825.537	211 234.977
	$(01^10)_f$	141 529.781	212 291.235
$D^{13}C^{15}N$	$(01^10)_e$	138 239.570	207 356.200
	$(01^10)_f$	138 927.703	208 388.246

[a] Reference [17].

Since the last term will make observable contributions to the rotational energy only for high J the first type of transitions discussed, with $\Delta J = +1$ and $|l| = 1$, may be adequately represented by [15]

$$\nu_{\pm} = 2(B_v + 2D_v)(J+1) - 4D_v(J+1)^3 \pm \tfrac{1}{2}\{2q_0(J+1) - 4q_1(J+1)^3\}, \quad (4)$$

where B_v and D_v are the rotational and centrifugal distortion constant in the vibrational state. For the second type of transitions with, $\Delta J = 0$, the transition frequencies are [16]

$$\nu = q_0 J(J+1) - q_1 J^2(J+1)^2 + q_2 J^3(J+1)^3. \quad (5)$$

IV. Assignment and Discussion

In Tables 1 to 2 the measured frequencies ν_{obs} are listed. Using Eq. (5) the coupling constants and the calculated frequencies ν_{cal} were determined. These frequencies are extrapolated to higher and lower frequencies in order to have predictions in the radio frequency and in the millimeter wave region. In Table 3 all the coupling constants which were determined in this work are collected together with those of the isotopic species $H^{12}C^{14}N$ and $D^{12}C^{14}N$ reported in the literature [4]. Table 3 also contains l-type doubling constants as determined according to Eq. (4) from the l-type splitting of the rotational lines [5—7, 9, 17]. Table 4 lists the unpublished l-type doublet rotational lines of the isotopic species $H^{12}C^{15}N$ and $H^{13}C^{15}N$ and their deuterated analogs [17].

The empirical coupling constants are compared in Table 5 with the ab-initio values, which were obtained from calculations of the energy hypersurfaces by Hennig, Kraemer, and Diercksen [11]. These SCF-calculations were modified in several ways, which show differences in refinement. In the CI-SD case all single and double excitations from the occupied to the virtual molecular orbitals are included in the SCF-calculations, whereas in the CI-SDQ case contributions of unlinked clusters to

Table 5. Comparison of the experimental l-type coupling constants q_0 in MHz for various isotopic species of hydrogen cyanide in the (01^10) state with available values.

Isotopic species	Experimental value of q_0	Theoretical values of q_0 according to Hennig, Kraemer and Diercksen[d]				
		estimated theoretical value	deviation from the empirical value	CI-SD	q_0-values from CI-SDQ calculations	CI (corr.)
$H^{12}C^{14}N$	224.4766[a]	217.4	3.2%	203.0	205.2	212.4
$H^{13}C^{14}N$	214.8378[b]	208.1	3.1%	194.3	196.5	203.4
$H^{12}C^{15}N$	211.9440[b]	205.2	3.2%	191.6	193.7	200.5
$H^{13}C^{15}N$	202.3556[b]	196.0	3.1%	183.0	185.0	191.5
$D^{12}C^{14}N$	186.1916[a]	181.5	2.5%	169.4	171.6	177.2
$D^{13}C^{14}N$	182.2941[b]	177.8	2.5%	165.9	168.0	173.6
$D^{12}C^{15}N$	176.0807[b]	171.6	2.5%	160.2	162.2	167.6
$D^{13}C^{15}N$	172.0455[b]	167.8	2.5%	156.6	158.6	163.9
$T^{12}C^{14}N$	150.822[c]	147.3	2.3%	137.5	139.4	143.9
$T^{13}C^{14}N$	149.749[c]	146.4	2.2%	136.6	138.5	143.0
$T^{12}C^{15}N$	142.688[c]	139.3	2.4%	130.1	131.9	136.1
$T^{13}C^{15}N$	—	138.2	—	129.0	130.8	135.0

[a] Reference [4]. [b] Present work. [c] Corrected values of Reference [9]. [d] Reference [11].

the correlation energy are considered. The CI (corr.) case includes an empirical correction: The CI-SD bond distances are lengthened by $+0.1\%$ and the harmonic force constants reduced by 10%. From the experimental vibrational constants of the isotopic species $H^{12}C^{14}N$, $H^{13}C^{14}N$ and $D^{12}C^{14}N$ the force constants were calculated, which were used to calculate the vibrational constants for all isotopic species. In the column "estimated" the coupling constants are listed which were obtained from these vibrational constants. The authors expected that the deviations of the estimated coupling constants from the experimental values would lie in the range between 0.1 and 1.0 MHz. Indeed this deviation is greater than expected (several MHz). On the other hand the deviation of the pure theoretical values are even greater despite of the empirical correction.

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[1] D. H. Rank, G. Skorinko, D. P. Eastman, and T. A. Wiggins, J. Opt. Soc. Amer. **50**, 421 (1960).
[2] W. W. Brim, J. M. Hoffman, H. H. Nielsen, and K. N. Rao, J. Opt. Soc. Amer. **50**, 1208 (1960).
[3] A. G. Maki and L. R. Blaine, J. Mol. Spectrosc. **12**, 45 (1964).
[4] A. G. Maki and D. R. Lide, J. Chem. Phys. **47**, 3206 (1967).
[5] G. Winnewisser, A. G. Maki, and D. R. Johnson, J. Mol. Spectrosc. **39**, 149 (1971).
[6] A. G. Maki, J. Phys. Chem. Ref. Data **3**, 221 (1974).
[7] F. C. DeLucia and P. A. Helminger, J. Chem. Phys. **67**, 4262 (1977).
[8] T. Törring, Z. Physik **161**, 179 (1961).
[9] F. C. DeLucia, J. Mol. Spectrosc. **55**, 271 (1975).
[10] E. F. Pearson, R. A. Creswell, M. Winnewisser, and G. Winnewisser, Z. Naturforsch. **31a**, 1394 (1976).
[11] P. Hennig, W. P. Kraemer, and G. H. F. Diercksen, A Compilation of Theoretical Spectroscopic Constants and Rotational-Vibrational Transition Frequencies for the Isoelectronic Series of Linear Triatomic Molecules HCN, HNC, HCO^+, HOC^+, HNN^+ Obtained from *Ab-Initio*-Calculated Energy Hypersurfaces, Max-Planck-Institute for Physics and Astrophysics/ PAE Astro 135, München 1977.
[12] J. M. Brown, J. T. Hougen, K. P. Huber, J. W. C. Johns, I. Kopp, H. Lefebre-Brion, A. J. Merer, D. A. Ramsay, J. Rostas, and R. N. Zare, J. Mol. Spectrosc. **55**, 500 (1975).
[13] W. Gordy and R. L. Cook, Microwave Molecular Spectra, Volume IX, Part II, Technique of Organic Chemistry, Arnold Weissberger (Editor), Interscience Publisher, New York 1970.
[14] H. H. Nielsen, J. Phys. Radium **15**, 601 (1954).
[15] M. Winnewisser and B. P. Winnewisser, Z. Naturforsch. **26a**, 128 (1971).
[16] M. Winnewisser and H. K. Bodenseh, Z. Naturforsch. **22a**, 1724 (1967).
[17] M. Winnewisser and R. A. Creswell, private communication.