ASTRONOMY
AND
ASTROPHYSICS

Letter to the Editor

Laboratory rotational spectrum of CN in the 1 THz region

E. Klisch[1], Th. Klaus[1], S.P. Belov[2], G. Winnewisser[1], and E. Herbst[3]

[1] I. Physikalisches Institut, Universität zu Köln, Zülpicher Straße 77, D-50937 Köln, Germany
[2] On leave of absence from the Microwave Spectroscopy Laboratory, Institute of Applied Physics, Nizhnii Novgorod, Russia 603024
[3] Departments of Physics and Astronomy, The Ohio State University, Columbus, OH 43210-1106, USA

Abstract. The rotational absorption spectrum of the cyanide radical, CN, in its $X^2\Sigma^+$ ground electronic state has been measured in the frequency region between 560 and 1020 GHz. The radical was produced in a DC discharge of methyl cyanide, CH_3CN, and molecular nitrogen, N_2. The measured lines should be of use to radio astronomers searching for CN in high excitation regions of the interstellar medium.

Key words: Molecular data - Methods : laboratory - Techniques : spectroscopic - ISM: clouds - ISM: molecules - Radio lines: ISM

1. Introduction

The history of the discovery of the cyanide radical, CN, dates back to the 1930's. First discovered in the optical region, both in the laboratory and in the interstellar medium, CN proved to be difficult to observe in the microwave region via its pure rotational spectrum. The lowest rotational transition, $N = 1 \rightarrow 0$, in its vibrational and electronic ground state was first detected by Jefferts et al. (1970) with associated fine and hyperfine structure towards the Orion A nebula. The CN radical was further studied at mm wavelengths by Turner & Gammon (1975) towards many galactic sources. It was not until 1977 that Dixon & Woods (1977) detected the laboratory microwave spectrum, observing the $v=0$ and $v=1$ vibrational states with several hours of integration. Since then, the rotational spectra of CN and the two isotopomers ^{13}CN and $C^{15}N$ have been reported from laboratory or interstellar measurements.

In 1983, Skatrud et al. observed the laboratory rotational spectrum of $^{12}C^{14}N$ in the frequency range from
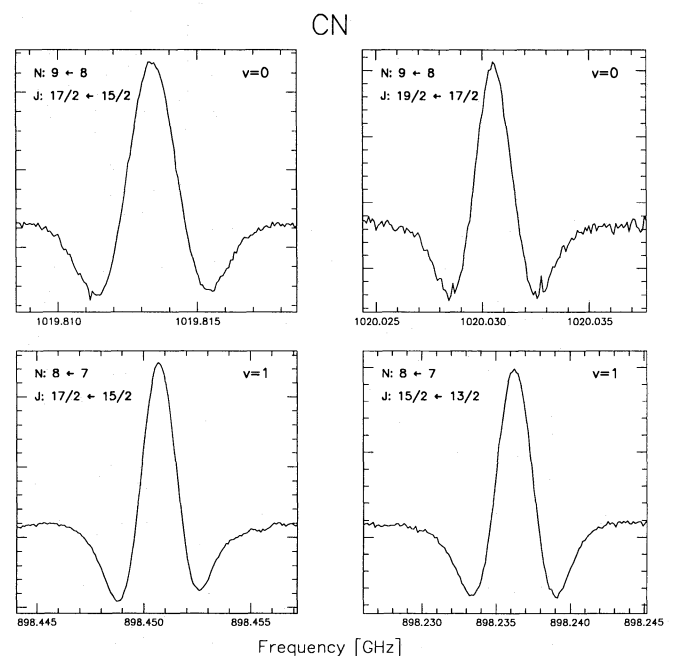
Fig. 1. Four newly measured rotational transitions of the CN radical

220 to 453 GHz up to the $v=3$ state and presented an accurate set of molecular constants. Shortly thereafter, Bogey et al. (1984) observed the millimeter wave spectrum of $^{13}C^{14}N$, which was subsequently detected in three galactic sources (Gerin et al. 1984). Based on the isotopic dependence of the molecular constants obtained in these previous studies, the frequencies of the first three rotational transitions of the isotopomer $C^{15}N$ were predicted and the $N = 1 \rightarrow 0$ and $N = 2 \rightarrow 1$ hyperfine patterns were subsequently detected towards Orion A (Saleck et al. 1993, 1994) and several other interstellar sources (R. Simon, private communication). On the basis of the astronomical data, Saleck et al. (1994) predicted the rotational spectrum of CN in its ground state up to 1 THz. Recent high spatial resolution measurements of the CN $N = 3 \rightarrow 2$ emission from the Orion Bar region (R.Simon, J.Stutzki

Table 1. Newly measured transition frequencies of CN in the $X^2\Sigma^+$ state.

N'	J'	$\leftarrow$	N''	J''	v	$\nu[MHz]$	$obs. - calc.[MHz]$	$E_{up}[cm^{-1}]$	$A \times 10^3[s^{-1}]$
5.0	4.5		4.0	3.5	0	566 730.630(600)	+ 0.279	56.705	1.980
5.0	5.5		4.0	4.5	0	566 946.974(450)	− 0.117	56.745	2.027
6.0	5.5		5.0	4.5	0	680 047.255(600)	− 0.048	79.389	3.498
6.0	6.5		5.0	5.5	0	680 264.051(300)	− 0.103	79.436	3.556
7.0	6.5		6.0	5.5	0	793 336.447(400)	+ 0.016	105.852	5.640
7.0	7.5		6.0	6.5	0	793 553.406(300)	− 0.127	105.906	5.707
8.0	7.5		7.0	6.5	0	906 593.388(200)	+ 0.035	136.093	8.510
8.0	8.5		7.0	7.5	0	906 810.484(200)	− 0.059	136.154	8.587
9.0	8.5		8.0	7.5	0	1 019 813.480(300)	+ 0.125	170.110	12.215
9.0	9.5		8.0	8.5	0	1 020 030.603(200)	− 0.129	170.179	12.303
6.0	5.5		5.0	4.5	1	673 779.808(550)	− 0.040	78.657	3.403
6.0	6.5		5.0	5.5	1	673 994.150(400)	− 0.219	78.704	3.458
7.0	6.5		6.0	5.5	1	786 024.944(1000)	+ 2.464	104.876	5.485
7.0	7.5		6.0	6.5	1	786 238.714(300)	+ 0.028	104.930	5.551
8.0	7.5		7.0	6.5	1	898 236.162(300)	+ 0.116	134.838	8.277
8.0	8.5		7.0	7.5	1	898 450.840(200)	+ 0.025	134.899	8.352

and G.Winnewisser, 1995 in preparation) reveal that CN provides an excellent tracer for dense photon-dominated regions (PDR's). In the Orion Bar, CN occurs in a thin layer, sandwiched between CS emission and vibrationally excited H_2, which faces the ionized region. In order to investigate the chemical structure of this dense PDR, Hogerheijde et al. (1995) observed the source in many different molecules at five positions along a strip crossing the Bar. The existence of CN in excited regions suggests the need for the extension of its known microwave spectrum toward higher frequencies.

In the present paper we report for the first time laboratory measurements of the higher rotational transitions of CN in the frequency region 560 to 1020 GHz. Although we have measured rotational transitions in vibrational states through v=7, we report here the rotational transitions in the lowest two vibrational states (v=0 and v=1) since these are of most interest for radioastronomers. The spectra for the vibrationally excited states up to v=7 will be published elsewhere.

2. Experimental

The essential parts of the Cologne terahertz spectrometer (Winnewisser et al. 1994) are the high-frequency, broadband tunable backward wave oscillators (BWO's) supplied by the ISTOK Research and Production Company, Moscow region, Russia. The BWO's are frequency and phase stabilized to the higher harmonics of a 78-118 GHz frequency synthesizer, supplied by the Institute of Electronic Measurements, KVARZ, located in Nizhnii Novgorod, Russia.

Our terahertz spectrometer was used in combination with a newly constructed, cooled, free space DC discharge cell. To optimize the production of CN, we monitored the intensity of the $N = 1 \leftarrow 0$ transition at 113.5 GHz by using the frequency synthesizer as power source while comparing different X-N_2 gas mixtures in the discharge, with X = methyl cyanide, CH_3CN, vinyl cyanide, CH_2CHCN, and CO. Methyl cyanide with N_2 gave the best CN yield at a total pressure of 60 μbar and a discharge current of about 100 mA. In the low frequency region, it was necessary to cool the discharge by flowing liquid nitrogen through the copper jacket attached to the cell walls since low temperatures increase the population of the lower energy levels. For the higher frequency transitions reported here, the CN signal was detectable at room temperature due mainly to the increase of the absorption coefficient with frequency as $\sim \nu^3$. Indeed, cooling of the cell showed no strong effect on the line intensities. Fig. 1 displays a few selected transitions in the terahertz region.

3. Theory and Analysis

The electronic ground state of CN is of $^2\Sigma^+$ symmetry. The Hamiltonian H describing the CN rotational energy levels in the ground electronic state consists of three parts:

$$H = H_{rot} + H_{fs} + H_{hfs},$$

where the subscripts rot, fs, and hfs refer to the rigid-body rotational, fine structure, and hyperfine structure contributions, respectively. The Hamiltonian is evaluated in a Hund's case (b_{β_J}) (Townes & Schawlow 1955) representation, in which the rigid-body angular momentum $\mathbf{N}$ and the electronic spin angular momentum $\mathbf{S}$ first couple

together to form a resultant **J**, which then couples with the nuclear spin angular momentum **I** to form the total angular momentum **F**:

$$\mathbf{J} = \mathbf{N} + \mathbf{S} \quad \text{and} \quad \mathbf{F} = \mathbf{J} + \mathbf{I}.$$

Because H_{rot} yields the largest contribution, the energy levels are first ordered according to the rotational quantum number N. The fine structure, arising from the coupling of the electron spin ($S = 1/2$) with the rigid-body rotation, leads to the so-called ρ-type doublet structure, with levels characterized by quantum numbers N and $J = N \pm 1/2$. In addition, for the lower N, J levels, the hyperfine contributions of the nitrogen nucleus - both magnetic dipole and electric quadrupole - have to be considered. Since the nuclear spin quantum number of the nitrogen nucleus $I = 1$, the values of the total angular momentum quantum number F are $J, J \pm 1$.

The matrix elements for H used in the Hund's case (b_{β_J}) representation are

$$\langle N'(S = \tfrac{1}{2})(I = 1)J'F \mid \hat{H} \mid N(S = \tfrac{1}{2})(I = 1)JF \rangle$$

$$= \{ [B - D\,N(N+1)]\,N(N+1)$$

$$+ \gamma\,\frac{1}{2}\,[J(J+1) - N(N+1) - \frac{3}{4}] \}\,\delta_{N',N}\,\delta_{J',J}$$

$$+ 3\,(-)^{J'+F+1}\,\sqrt{(2J+1)(2J'+1)}\,\left\{ \begin{matrix} F & J' & 1 \\ 1 & 1 & J \end{matrix} \right\}$$

$$\times \left\{ b_F\,(-)^{N+J+\frac{3}{2}} \left\{ \begin{matrix} \tfrac{1}{2} & J' & N \\ J & \tfrac{1}{2} & 1 \end{matrix} \right\} \delta_{N',N} \right.$$

$$- t\,\sqrt{30}\,(-)^{N'}\,\sqrt{(2N+1)(2N'+1)}$$

$$\times \left. \left\{ \begin{matrix} \tfrac{1}{2} & \tfrac{1}{2} & 1 \\ N' & N & 2 \\ J' & J & 1 \end{matrix} \right\} \left(\begin{matrix} N' & 2 & N \\ 0 & 0 & 0 \end{matrix} \right) \right\}$$

$$+ eQq\,(-)^{N+N'+J'+\frac{5}{2}}\,\sqrt{\frac{5}{24}}$$

$$\times \sqrt{(2N+1)(2N'+1)}\,\left\{ \begin{matrix} F & J' & 1 \\ 2 & 1 & J \end{matrix} \right\} \left\{ \begin{matrix} N' & J' & \tfrac{1}{2} \\ J & N & 2 \end{matrix} \right\}$$

$$\times \left(\begin{matrix} N' & 2 & N \\ 0 & 0 & 0 \end{matrix} \right) \Big\}.$$

The measured frequencies ν along with quantum numbers N, J, residuals (observed-calculated frequencies), upper state energies (cm^{-1}) and Einstein A-coefficients (s^{-1}) are listed in Table 1. The quoted uncertainties for the measured transition frequencies reflect the partially unresolved hyperfine structure and not the experimental uncertainties, which is for unblended lines below 10 kHz. The transition at 787024.944 MHz was measured with a free

Table 2. Electronic ground state rotational parameters

Parameter	$v = 0$	$v = 1$	Unit
B_v	56 693.470 3 (17)	56 171.102 0 (22)	MHz
D_v	192.221 (21)	192.478 (37)	kHz
γ_v	217.498 8 (57)	215.070 9 (93)	MHz
b_{F_v}	− 13.857 (14)	− 12.992 (17)	MHz
t_v	20.127 (12)	20.198 (14)	MHz
eQq_v	− 1.275 (32)	− 1.178 (34)	MHz

running BWO and is not included into the fit. The Einstein A-coefficients $A_{m \to n}$ are obtained from the formula

$$A_{m \to n} = \frac{64\pi^4 \nu_{mn}{}^3}{3hc^3}\,\mu^2\,(2J'+1) \left\{ \begin{matrix} N' & J' & S \\ J & N & 1 \end{matrix} \right\}^2$$

$$\times (2N'+1)(2N+1) \left(\begin{matrix} N' & 1 & N \\ 0 & 0 & 0 \end{matrix} \right)^2,$$

where $\mu = 1.45\,D$ is the permanent electric dipole moment of CN (Thomson & Dalby 1968). The predictions based on astronomical data by Saleck et al. (1994) agree with our new laboratory measurements to within less than 160 kHz. The molecular constants listed in Table 2 have been derived from global fits to our and previous data for the $v = 0$ and 1 states (Skatrud et al. 1983; Johnson et al. 1984). The hyperfine constants b_{F_v}, t_v and eQq_v are obtained from low N transitions not reported here. The inclusion of the higher N transitions has improved the centrifugal distortion constant D_v; the other constants are in very good agreement with literature values. The numbers in parantheses denote 1σ uncertainties.

4. CN in different interstellar sources

The CN radical is a common interstellar molecule which is found in a variety of sources. In the ζ Oph diffuse cloud, the fractional abundance of CN with respect to the overall gas density is observed to be 6×10^{-9} (Meyer & Jura 1985). A compilation of a large number of diffuse sources by Federman et al. (1994) reveals similar fractional abundances for CN. In the TMC-1 dark cloud ($n = 10^4$ cm^{-3}, $T = 10$ K), the fractional abundance of CN is 3×10^{-8} (Irvine et al. 1987) while in the extended ridge of the Orion Nebula ($n = 10^5$ cm^{-3}, $T = 50$ K), its fractional abundance is 3×10^{-9} (Blake et al. 1987). The observation that the fractional abundance of CN is fairly similar in diffuse and dense environments has been reproduced by a recent model calculation with sophisticated radiative transfer codes (Lee, Herbst, Roueff, Pineau des Forêts & Le Bourlot, in preparation).
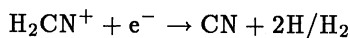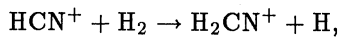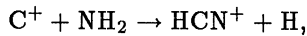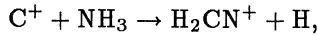
The CN radical in diffuse clouds (Federman et al. 1994) is produced by reactions such as

$$CH + N \rightarrow CN + H$$

and

$$C_2 + N \rightarrow CN + C,$$
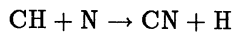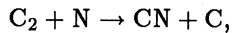
while in dense clouds the additional syntheses

$$C^+ + NH_3 \rightarrow H_2CN^+ + H,$$

$$C^+ + NH_2 \rightarrow HCN^+ + H,$$

$$HCN^+ + H_2 \rightarrow H_2CN^+ + H,$$

$$H_2CN^+ + e^- \rightarrow CN + 2H/H_2$$

are important. The CN radical is depleted by photodissociation in diffuse clouds, and chemically in diffuse and dense clouds, with the principal destruction reaction a neutral-neutral one:

$$CN + O \rightarrow CO + N.$$
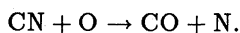
Gas phase model results for dense clouds are especially sensitive to the unknown rate of the CN + O reaction (Herbst et al. 1994).

Since CN is detected in diffuse environments rich in photons, it is perhaps not surprising that it also occurs as a salient feature in the Orion Bar source, a well-studied photon-dominated region (Hogerheijde et al. 1995; R. Simon, J. Stutzki, and G. Winnewisser, in preparation). Several PDR models contain predictions for CN. Sternberg & Dalgarno (1995), in their detailed steady-state treatment of a dense PDR, calculate that CN has its maximum fractional abundance at $A_v = 1 - 2^m$ from the onset. This model also predicts that CS occurs farther from the ionized region, at $A_v \approx 8$, in agreement with our observations. At such high extinctions, the CN radical is converted into HCN. In the model of Jansen et al. (1995), CN peaks at $A_v = 2 - 3^m$ while CS has a subsidiary peak at $A_v = 2 - 3^m$ with its dominant contribution at high visual extinction. The CN profile in the Bar source may be affected both by geometrical and temporal considerations.

References

Blake, G. A., Sutton, E. C., Masson, C. R., Phillips, T. G., 1987, ApJ 315, 621

Bogey, M., Demuynck, C., Destombes, J. L., 1984, Canadian J. Phys. 62, 1248

Dixon, T. A., Woods, R. C., 1977, J. Chem. Phys. 67, 3956

Federman, S. R., Strom, C. J., Lambert, D. L., Cardelli, J. A., Smith, V. V., Joseph, C. L., 1994, ApJ 424, 772

Gerin, M., Combes, F., Encrenaz, P., Linke, R., Destombes, J. L., Demuynck, C., 1984, A&A 136, L17

Herbst, E., Lee, H.-H., Howe, D. A., Millar, T. J., 1994, MNRAS 268, 335

Hogerheijde, M. R., Jansen, D. J., van Dishoeck, E. F., 1995, A&A 294, 792

Irvine, W. M., Goldsmith, P. F., Hjalmarson, Å., 1987, in Interstellar Processes, ed. D. J. Hollenbach & H. A. Thronson (Dordrecht: Reidel), 561

Jansen, D. J., van Dishoeck, E. F., Black, J. H., Spaans, M., Sosin, C., 1995, A&A in press

Jefferts, K. B., Penzias, A. A., Wilson, R. W., 1970, ApJ 161, L87

Johnson, N. A., Alexander,N. L., Hertel,I., Lineberger, W. C., 1984, Chem. Phys. Lett. 105, 374

Meyer, D. M., Jura, M., 1985, ApJ 297, 119

Saleck, A. H., Simon, R., Schneider, N., Winnewisser, G., 1993, ApJ 414, L133

Saleck, A. H., Simon, R., Winnewisser, G., 1994, ApJ 436, 176

Skatrud, D. D., De Lucia, F. C., Blake, G. A., & Sastry, K. V. L. N., 1983, J. Mol. Spectrosc. 99, 35

Sternberg, A., Dalgarno, A., 1995, ApJS 99, 565

Thomson, R., Dalby, F. W., 1968, Can. J. Phys. 46, 2815

Townes, C. H., Schawlow, A. L., 1955, Microwave Spectroscopy (London: McGraw-Hill)

Turner, B. E., Gammon, R. H., 1975, ApJ 198, 71

Winnewisser, G., Krupnov, A. F., Tretyakov, M. Yu., Liedtke, M., Lewen, F., Saleck, A. H., Schieder, R., Shkaev, A. P., Volokhov, S. V., 1994, J. Mol. Spectrosc. 165, 294