Millimeter and submillimeter wave spectroscopy of HNC and DNC in the vibrationally excited states

Toshiaki Okabayashi and Mitsutoshi Tanimoto
Department of Chemistry, Faculty of Science, Shizuoka University, 836 Oya, Shizuoka 422, Japan

(Received 31 March 1993; accepted 24 May 1993)

The rotational transitions of hydrogen isocyanide (HNC) and deuterium isocyanide (DNC) in the vibrationally excited states as well as in the ground states were observed in the millimeter and submillimeter wave region. These compounds were generated in a dc glow discharge plasma containing hydrogen (or deuterium), nitrogen, and carbon atoms. The stretching vibrational modes, ν_1 and ν_3 states, were selectively excited in the discharge plasma; on the other hand, the bending mode ν_2 state was thermally populated at the cell temperature. The precise rotational, centrifugal distortion and *l*-type doubling constants were obtained for all of the first vibrationally excited states as well as the ground states. The experimental equilibrium rotational constants B_e are 45 496.7769(45) and 38 207.7217(105) MHz for HNC and DNC, respectively, where uncertainties correspond to one standard deviation. The equilibrium internuclear distances are also determined to be r_e (H–N) = 0.996 0643(29) Å and r_e (N≡C) = 1.168 3506(16) Å.

INTRODUCTION

Since the first detection of an interstellar millimeter wave emission line U90.7,[1,2] which has subsequently been assigned to the $J=0$–1 transition of the HNC molecule, microwave studies have been performed on HNC and its isotopic species DNC in several laboratories. Creswell and his co-workers[3,4] observed the rotational transitions in the ground vibrational state of not only the parent but also the rare isotopic species in the products of the reaction of methyl iodide with excited nitrogen and determined the substitution molecular structure. Saykally *et al.*[5] independently observed the $J=1$–0 transition of HNC in dc glow discharges through mixtures of cyanogen and hydrogen, cyanogen and acetylene, or nitrogen and acetylene. Blackman *et al.*[6] also measured the $J=1-0$ lines of HNC and DNC generated by heating samples of HCN or DCN to temperatures of about 1000 K, and determined the electric dipole moment (3.05±0.1 Debye) from Stark effect measurements. Recently, Woods[7] reported the experimental equilibrium structure of HNC.

In the infrared region the first observation was reported by Milligan and Jacox[8,9] following the photolysis of CH_3N_3 or HCN in an Ar matrix at 4 K. The vibrational–rotational spectrum of the ν_1 fundamental band of gaseous HNC was observed in emission in the reaction of active nitrogen with various molecules by Arrington and Ogryzlo[10] with a low resolution spectrometer. Maki and Sams[11] measured with a high resolution grating spectrometer not only the ν_1 bands but also accompanying ν_2 hot bands of HNC and DNC in equilibrium with HCN (or DCN) at high temperature. The most detailed study of HNC, which was generated by reacting the products of a microwave discharge of N_2 with CH_3Br, was carried out by Burkholder *et al.*[12] with a high resolution Fourier transform infrared (FTIR) spectrometer. They observed the ν_1, ν_2, and ν_3 fundamental bands and determined accurate molecular constants. However there has been reported no spectroscopic data for the ν_3 state of DNC.

The present paper reports measurements of the rotational transitions in all of the first excited states as well as in the ground state of HNC and DNC in the millimeter and submillimeter wave region. The observed rotational spectra were analyzed by the least-squares method for each vibrational state to obtain precise values of the rotational, centrifugal distortion, and *l*-type doubling constants. Using the rotational constants thus obtained, we determined the vibration–rotation constants and the equilibrium rotational constants of HNC and DNC. Moreover, we also determined the equilibrium structure from two equilibrium rotational constants.

INSTRUMENT

Figure 1 shows a schematic diagram of the microwave spectrometer newly constructed in Shizuoka University and used in the present experiment. As microwave sources, OKI millimeter wave klystrons are employed in the region below 130 GHz. The millimeter wave radiation in the 200 to 280 GHz region is generated by multiplying the output of a klystron using a tripler (Millitech MU-3-03-T1). The tripler also provides spurious fourth harmonic power which is adequate as the source in the submillimeter wave region above 300 GHz. The microwave transmitted through a free space cell is detected by a liquid-He cooled InSb hot electron detector (QMC QFI/2).

The millimeter wave klystron is repetitively scanned in frequency by applying a sawtooth of 10 Hz to its reflector electrode. The frequency of the klystron is monitored by referring to harmonics of an X-13 centimeter wave klystron, which is phase locked by a microwave stabilizer (Dymec DY2650A) to the output of a synthesized signal generator (HP8656A). A microwave counter (Advantest R5372) which counts the X-13 frequency and the signal generator are controlled by a 16-bit personal computer

 0021-9606/93/99(5)/3268/4/$6.00

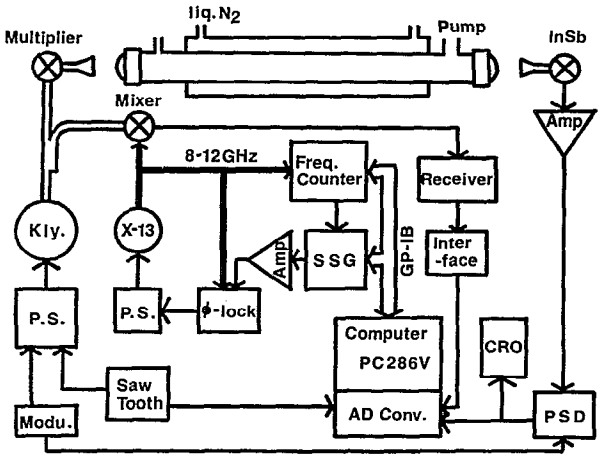

FIG. 1. A schematic diagram of the microwave spectrometer.

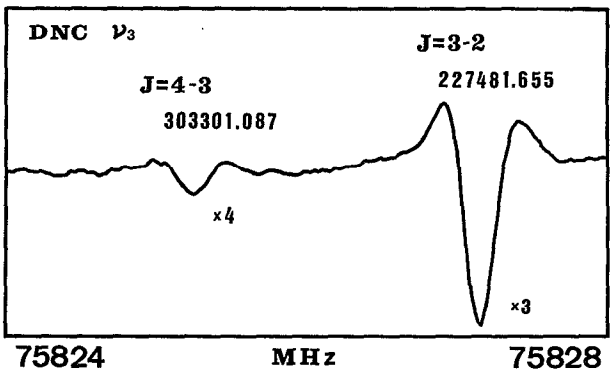

FIG. 2. The millimeter and submillimeter wave spectra of rotational transitions $J=3$–2 and $J=4$–3 in the ν_3 excited state of DNC. The horizontal axis represents the klystron fundamental frequency. The frequency given over the absorption lines is the product of the klystron frequency and harmonics which is also indicated. The signal was accumulated for 10 s.

(EPSON PC286V) through a GPIB interface. Beat notes between the output of two klystrons are detected by a radio-frequency receiver (Nissin Electronic NRR-201A).

The microwave is frequency modulated to a full width of a few hundred kHz by applying a bipolar square wave of 50 kHz to the reflector of the millimeter wave klystron. A phase sensitive detector (NF LI-517) is operated at 100 kHz with 1.25 ms time constant, and the recorded signal had a second derivative lineshape.

The PSD output, the shaped beat notes from the receiver, and the monitor signal from the sawtooth are fed into a 12 bit A/D converter. After digitization, the PSD output is allocated to 256 data points for every scan, the start and end of which are decided by voltages of the sawtooth monitor signal. The positions of a plus and a minus beat note are employed to calculate the frequency scale for the absorption signal by interpolation. The process is repeated for every scan to accumulate for several minutes. The computer software is mainly written in BASIC language and partly complemented by C language which is suitable for controlling hardware.

The free-space-type absorption cell is of 2 m long and 10 cm o.d. Pyrex glass tube, sealed with a pair of Teflon lenses of the focal length of about 25 cm at both ends. The cell is evacuated by a mechanical booster pump (Shinko Seiki) of 2500 *l*/min. A pair of cylindrical stainless steel electrodes are inserted at each end of the cell for discharge. The cell is surrounded by a cooling jacket made of copper with a soldered pipe through which liquid nitrogen is circulated. Adjustment of the rate of the liquid nitrogen flow can control the cell temperature to the desired value between 77 K and room temperature. The cell is installed in a thick styrofoam block for thermal insulation.

EXPERIMENT

HNC and DNC molecules were directly generated in the absorption cell by a dc glow discharge. In order to avoid interfering lines originating from starting materials or generated by-products, we employed several reaction systems:

for HNC

$$H_2C{=}CHCN\ (20\ \text{mTorr}){+}H_2\ (10\ \text{mTorr}) + He\ (30\ \text{mTorr}), \quad \text{(A)}$$

$$CH_3CN\ (30\ \text{mTorr}){+}He\ (30\ \text{mTorr}), \quad \text{(B)}$$

or

$$CH_3I\ (25\ \text{mTorr}){+}N_2\ (25\ \text{mTorr}) \quad \text{(C)}$$

and for DNC

$$CD_3CN\ (30\ \text{mTorr}){+}He\ (30\ \text{mTorr}), \quad \text{(D)}$$

or

$$CD_3I\ (25\ \text{mTorr}){+}N_2\ (25\ \text{mTorr}). \quad \text{(E)}$$

We mainly chose the (A), (B), or (D) reaction systems because in these systems the line shape of the target molecule spectrum was narrower and there were less interfering lines than in the (C) or (E) reaction systems. The generation condition was determined by monitoring the line intensity in the ground state. The discharge current was adjusted around 300 mA and the temperature of the cell was kept at around 210 K. The line strength of HNC and DNC lines was not sensitive to the discharge conditions, such as the cell temperature, the discharge current and the sample pressure.

Based on the prediction from the infrared result,[11,12] we readily observed the rotational transitions in the ν_1, ν_2, and ν_3 excited states of HNC, and in the ν_1 and ν_2 states of DNC. The transition frequencies of DNC in the ν_3 state were predicted by assuming that the vibration–rotation constant α_3 is equal to that of DNN^+ (239 MHz),[13] since DNC and DNN^+ have same electronic structure and similar rotational constants in the ground state (38 152 MHz and 38 554 MHz, respectively). We searched for the ν_3 lines on a cathode ray oscilloscope and easily detected them at the position of $\alpha_3=238$ MHz (Fig. 2).

Under the experimental conditions described above, the line intensities of the ν_1 and ν_3 states were found to be

TABLE I. Observed transitions of HNC and DNC (MHz).[a]

State	J=1–0	J=2–1	J=3–2	J=4–3
HNC				
Ground	90 663.593(9)[b]	181 324.758(−8)[b]	271 981.142(2)	362 630.303(0)
ν_1			270 185.386(−20)	360 236.110(15)
$\nu_2(e)$	···		271 924.156(−13)	362 554.351(9)
(f)	···		273 869.532(−13)	365 147.495(9)
ν_3	89 993.197(12)		269 969.964(−9)	359 948.787(3)
DNC				
Ground	76 305.727(7)[b]	152 609.774(1)[b]	228 910.489(−6)	305 206.219(2)
ν_1	75 704.545(38)[d]		227 106.935(−13)	302 801.600(5)
$\nu_2(e)$	···		229 327.206[50][c]	
(f)	···		231 070.095[50][c]	308 084.675[50][c]
ν_3	75 829.460(11)		227 481.655(−8)	303 301.087(3)

[a]Values in parentheses represent the residual (Obs.–Calc.) in kHz.
[b]From Refs. 3 and 4.
[c]Estimated experimental error.
[d]Less weighted because of poor S/N ratio.

abnormally strong. The effective vibrational temperature was estimated from the line intensities; 1300–1600 K for the ν_1 and ν_3 states and 230 K for the ν_2 state. This means that the stretching mode was selectively excited in the discharge plasma, and that the bending mode, on the other hand, was thermally populated.

ANALYSIS

Table I lists the measured rotational transitions between J=1–0 and J=4–3 for two isotopomers. The observed spectral lines were analyzed using the standard rotational energy formula for a linear molecule:

$$E_{v,J}=B_v[J(J+1)-l^2]-D_v[J(J+1)-l^2]^2 \pm\tfrac{1}{2}[q+q_J J(J+1)]J(J+1), \quad (1)$$

where v and l are the quantum numbers of the vibrations. The value of l is fixed to one in the ν_2 state and to zero in the other states. The term of q and q_J in Eq. (1) accounts for the l-type doubling in the ν_2 excited state with the + and − signs for f and e state, respectively.

The transition frequencies were subjected to least-squares analysis to give the molecular constants summarized in Table II. The observed transitions in the ν_2 state of DNC are so limited that we could not determine the molecular constants accurately. The present molecular constants are in good agreement with those of the previous infrared work[11,12] but are more precise.

DISCUSSION

The stretching vibrational modes of HNC, the ν_1 and ν_3 states, were selectively excited in the discharge plasma. The phenomenon like this case has been reported; for HBO (Refs. 14 and 15) in the discharge plasma of B_2H_6, O_2, and He mixture, for HCO^+ (Ref. 16) in the discharge plasma of CO, H_2 and He mixtures, and for HCN[17] in the active laser plasma of HCN. The effective vibrational temperature of the stretching modes is estimated from the measurement of the relative intensities, that is 1000–2000 K for HBO,[14] 700–900 K for HCO^+,[16] and 1300–1600 K for HNC. The bending vibrational mode, the ν_2 state, however, is almost thermally populated; 500 K for HBO,[14] 370 K for HCO^+,[16] and 230 K for HNC.

In the present study we have determined the rotational constants in the vibrationally excited states. These allow us to calculate the vibration–rotation constants, i.e., α_1 =299.3056(32), α_2=−152.4686(26), and α_3 =335.2003(53) MHz for HNC, and α_1=300.6081(111), α_2=−214.6486(85), and α_3=238.1349(47) MHz for DNC. The equilibrium rotational constants, taking into account α_v's but not higher order term γ_v's, are 45 496.7769(45) and 38 207.7217(105) MHz, respectively.

Equilibrium type (r_e) structure is determined from the equilibrium rotational constants of HNC and DNC using the conversion factor 505 379.05(31) u Å^2 MHz. A summary of r_e and r_s structures is given in Table III. The r_e bond length of NC is in good agreement with the r_s value: the difference between them is about 0.003 Å. However, the r_s-r_e value of the HN distance is about −0.01 Å,

TABLE II. Molecular constants of HNC and DNC.

	HNC	DNC	
B_0	45 331.9925(20)	38 152.9988(16)	MHz
D_0	100.144(77)	69.428(62)	kHz
B_1	45 032.6869(25)	37 852.3907(110)	MHz
D_1	99.219[c]	68.481(398)	kHz
B_2	45 484.4611(16)	38 367.6474[83][b]	MHz
D_2	103.231[c]	75.352[676][b]	kHz
q	324.340(13)	290.593[17][b]	MHz
q_J	−6.17(47)	−6.17[d]	kHz
B_3	44 996.7922(49)	37 914.8639(44)	MHz
D_3	99.819(181)	69.639(162)	kHz

[a]Values in parentheses represent one standard deviation in units of the last digit.
[b]Estimated value from experimental error.
[c]From Ref. 10. Fixed in the analysis.
[d]Assumed value.

TABLE III. r_e and r_s structure of HNC (Å).

	r(H–N)	r(N≡C)
r_e	0.996 0643(29)	1.168 3506(16)[a]
	0.996 959(1450)	1.168 363(226)[b]
	0.993 57(117)	1.164 53(28)[c]
r_s	0.985 884(120)	1.172 055(7)[b]
	0.986 07(9)	1.171 68(22)[c]

[a]This work. The uncertainties are derived from one standard deviation in the B_e value. The accuracy is estimated to be about two orders worse than the value in parentheses.
[b]From Ref. 7.
[c]From Ref. 4.

which is one order of magnitude larger than that of the NC distance. In most cases, the bond lengths of both r_e and r_s structures have similar values. The anomaly found here strongly suggests the large amplitude bending vibration of HNC molecule.

The difference between r_s and r_e structure reflects the residual effects of zero-point vibration; the bending vibration tends to shorten the "average" bond length and the anharmonic stretching vibration to lengthen it. If the hydrogen atom is undergoing a large amplitude bending vibration, the difference between the r_s and r_e structure will have a large negative value, as is found here for the hydrogen–nitrogen distance of HNC. In fact, for HNC the difference between r_s(H–X) and r_e(H–X) is −0.01 Å, which is much larger than those of isoelectronic molecules, −0.002 Å for HNN^+,[7] −0.003 Å for HCN,[7] −0.004 Å for HCO^+,[7] and −0.0007 Å for HBO;[15] these molecules do not have large amplitude vibrations.

The bending potential function remarkably affects an l-type doubling constant. Table IV shows l-type doubling constants of HNC (and DNC) and the isoelectronic molecules.[15,16,18–21] Generally, not only the "stiffer" bending potential but also the smaller rotational constant will cause the smaller l-type doubling constant. Since all molecules in Table IV except HBO (and DBO) have similar rotational constants, the magnitude of the l-type doubling constant directly reflects the relative "stiffness" of the bending vibration, $HCO^+ > HCN > HNN^+ \gg HNC \gg HOC^+$. This order is also supported by *ab initio* calculation.[22] If the contribution of the rotational constant is removed, the resulting "stiffness" of the bending vibration of HBO will probably be close to that of HCN or HNN^+.

TABLE IV. Comparison of l-type doubling constants for isoelectronic molecules (MHz).[a]

	H species	D species	Ref.
HBO	181.995(11)[b]	144.139(2)[b]	15
HCO^+	211.7659(41)	171.020(11)	16
HCN	224.4766(2)	186.1916(3)	18
HNN^+	254.966(11)	218.084(78)	19,20
HNC	324.340(13)	290.593[17]	c
HOC^+	518.14(58)		21

[a]Values in parentheses represent one standard deviation in units of the last digit.
[b]^{11}B species.
[c]This work. See Table II.

The rotational transitions of the isomer HCN in the vibrationally excited states were observed in the molecular cloud Ori.KL and the circumstellar envelope IRC +10216.[23,24] Very recently an interferometric observation was carried out to constrain the location of the vibrationally excited HCN emmision region in IRC+10216.[25] The rotational, centrifugal distortion, and l-type doubling constants precisely determined in this work would enable the astrophysical detection of HNC molecule in the vibrationally excited states, as is carried out for the HCN molecule.

ACKNOWLEDGMENTS

We thank Professor Shuji Saito of Institute of Molecular Science and Dr. Satoshi Yamamoto of Nagoya University for their helpful suggestions in constructing the microwave spectrometer. We are also grateful to Hideki Sugiura and Takaaki Kanno for their assistance in making the instrument. The present study is supported by Grant-in-Aid for Scientific Research (Nos. 01470015, 01632512, and 04233107) from the Ministry of Education, Science and Culture.

[1] L. E. Snyder and D. Buhl, Bull. Am. Astron. Soc. **3**, 388 (1971).
[2] L. E. Snyder and D. Buhl, Ann. N. Y. Acad. Sci. **194**, 17 (1972).
[3] R. A. Creswell, E. F. Pearson, M. Winnewisser, and G. Winnewisser, Z. Naturforsch. **31a**, 221 (1976).
[4] E. F. Pearson, R. A. Creswell, M. Winnewisser, and G. Winnewisser, Z. Naturforsch. **31a**, 1394 (1976).
[5] R. J. Saykally, P. G. Szanto, T. G. Anderson, and R. C. Woods, Astrophys. J. **204**, L143 (1976).
[6] G. L. Blackman, R. D. Brown, P. D. Godfrey, and H. I. Gunn, Nature **261**, 395 (1976).
[7] R. C. Woods, Philos. Trans. R. Soc. London, Ser. A **324**, 141 (1988).
[8] D. E. Milligan and M. E. Jacox, J. Chem. Phys. **39**, 712 (1963).
[9] D. E. Milligan and M. E. Jacox, J. Chem. Phys. **47**, 278 (1967).
[10] C. A. Arrington and E. A. Ogryzlo, J. Chem. Phys. **63**, 3670 (1975).
[11] A. G. Maki and R. L. Sams, J. Chem. Phys. **75**, 4178 (1981).
[12] J. B. Burkholder, A. Sinha, P. D. Hammer, and C. J. Howard, J. Mol. Spectrosc. **126**, 72 (1987).
[13] S. C. Foster and A. R. W. Mckellar, J. Chem. Phys. **81**, 3424 (1984).
[14] Y. Kawashima, Y. Endo, K. Kawaguchi, and E. Hirota, Chem. Phys. Lett. **135**, 441 (1987).
[15] Y. Kawashima, Y. Endo, and E. Hirota, J. Mol. Spectrosc. **133**, 116 (1989).
[16] E. Hirota and Y. Endo, J. Mol. Spectrosc. **127**, 527 (1988).
[17] F. C. De Lucia and P. A. Helminger, J. Chem. Phys. **67**, 4262 (1977).
[18] A. G. Maki and D. R. Lide, Jr., J. Chem. Phys. **47**, 3206 (1967).
[19] W. C. Ho, C. J. Pursell, D. P. Weliky, K. Takagi, and T. Oka, J. Chem. Phys. **93**, 87 (1990).
[20] T. J. Sears, J. Chem. Phys. **82**, 5757 (1985).
[21] T. Amano, J. Mol. Spectrosc. **139**, 457 (1990).
[22] W. P. Kraemer and P. R. Bunker, J. Mol. Spectrosc. **101**, 379 (1983).
[23] L. N. Ziurys and B. E. Turner, Astrophys. J. **300**, L19 (1986).
[24] R. Lucas, A. Omont, S. Guilloteau, and Nguyen-Q-Rieu, Astron. Astrophys. **154**, L12 (1986).
[25] R. Lucas and S. Guilloteau, Astron. Astrophys. **259**, L23 (1992).