

## Microwave Spectra of $T^{12}C^{14}N$ , $T^{13}C^{14}N$ , and $T^{12}C^{15}N$ in the Ground and Excited Bending Vibrational States<sup>1</sup>

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Small concentrations of monomeric TCN have been produced by exchange of HCN and  $T_2O$  inside a quasi-free-space microwave absorption cell. A large number of rotational transitions of  $T^{12}C^{14}N$ ,  $T^{13}C^{14}N$ , and  $T^{12}C^{15}N$  in both the  $00^0_0$  and  $01^1_0$  vibrational states have been observed in the 100–500 GHz region. These measurements were made possible by the strong interaction between electromagnetic radiation and the rotational motion of molecules in this spectral region and the sensitivity and resolution of the phase-locked millimeter and submillimeter spectrometer used. The spectral constants which result from this work are (in MHz) for  $T^{12}C^{14}N$ :  $00^0_0$  state;  $B_0 = 30954.080(8)$ ,  $D_0 = 0.04382(10)$ ,  $01^1_0$  state;  $B_0 = 31080.410(5)$ ,  $D_0 = 0.04582(8)$ ,  $q_2^{(0)} = 150.809(7)$ ,  $q_2^{(1)} = 0.0041(2)$ , for  $T^{13}C^{14}N$ :  $00^0_0$  state;  $B_0 = 30591.036(7)$ ,  $D_0 = 0.04245(9)$ ,  $01^1_0$  state;  $B_0 = 30709.082(12)$ ,  $D_0 = 0.04437(16)$ ,  $q_2^{(0)} = 149.744(17)$ ,  $q_2^{(1)} = 0.0032(4)$ , for  $T^{12}C^{15}N$ :  $00^0_0$  states;  $B_0 = 30064.400(12)$ ,  $D_0 = 0.04119(14)$ ,  $01^1_0$  state;  $B_0 = 30186.560(8)$ ,  $D_0 = 0.04300(14)$ ,  $q_2^{(0)} = 142.674(12)$ ,  $q_2^{(1)} = 0.0042(4)$ .

### I. INTRODUCTION

The study of the tritium species of light, hydrogen-containing compounds makes possible the investigation of the effects of isotopic substitution over a significantly wider fractional mass range than any other substitution. In addition, many of the difficulties associated with the calculation of molecular parameters are significantly reduced for the tritium species because the increased mass of the vibrating system reduces the contributions of vibrational effects to these calculations (1).

Hydrogen cyanide is the lightest stable linear molecule and as such serves as an important benchmark for this class of molecules. However, because its rotational spectrum lies in the shorter millimeter and submillimeter region of the spectrum, only low  $J$  transitions of HCN and DCN have been observed with microwave techniques (2, 3, 4). These observations, combined with measurements of the direct  $l$ -type transitions which fall in the centimeter region of the spectrum (5, 6), have made possible the calculation of the molecular parameters of HCN and DCN. In this paper are reported the millimeter and submillimeter microwave spectra of  $T^{12}C^{14}N$ ,  $T^{13}C^{14}N$ , and  $T^{12}C^{15}N$  in both the ground and excited bending vibrational states. The large number of different rotational transitions observed, including high  $J$  transitions in both the ground and excited bending states, makes possible the calculation of both the rotational and  $l$ -type doubling con-

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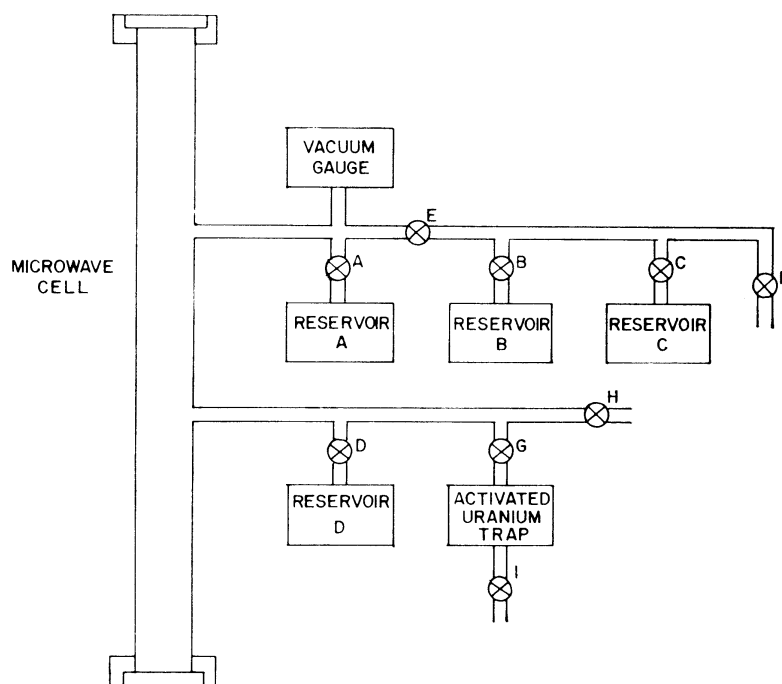


FIG. 2. Gas handling system and microwave cell.

The gas handling system and microwave cell are shown in Fig. 2. Except for the arm beyond valve E, the system is one which has been described in a study of  $T_2O$  (8). For this experiment, sample reservoir C was filled with either a mixture of 30%  $D^{13}C^{14}N$  and 70%  $D^{12}C^{14}N$  or 99%  $H^{12}C^{15}N$  through valve F from an external gas handling system. The arm between valves E and F, as yet uncontaminated by tritium, was evacuated through valve F, valve F closed, and the external vacuum system removed. This resulted in an evacuated, sealed system with DCN stored in reservoir C,  $T_2O$  stored in reservoir D, and reservoir A empty (reservoir B contained a sample for another experiment).

The only previous work on TCN, a low-resolution infrared study (9), was severely hampered both by the radioactivity of the large sample required (130 Ci) and by the rapid,  $\beta$ -induced polymerization of TCN into a trimer. Because of its large dipole moment and favorable partition function, TCN is a strong absorber in the millimeter and submillimeter region of the microwave spectrum. As a result, only small concentrations were required for this work and these concentrations could be produced by exchange of the hydrogen or deuterium species of hydrogen cyanide and  $T_2O$  inside the microwave absorption cell. Exchange was complete in approximately one minute and the sample concentration remained stable for the duration of a data run (approximately six hours). However, once this sample was removed from the microwave cell by cryogenic trapping into reservoir A, it was necessary to prepare a new sample by exchange as it was not possible to return a detectable concentration of TCN to the absorption cell from reservoir A. Optimum pressure is on the order of  $50 \mu m$  for transitions at 300 GHz. Although strong signals were observed, the fraction of absorbed microwave power indicates that less than 1% of the sample was monomeric TCN.

TABLE I  
Rotational transition frequencies of  $\text{HCN}(00^0)$

Transition	$^{12}\text{C}^{14}\text{N}$		$^{13}\text{C}^{14}\text{N}$		$^{12}\text{C}^{15}\text{N}$	
	Observed	Calculated	Observed	Calculated	Observed	Calculated
$J=0 \rightarrow 1$	206.9168	206.9168	206.9168	206.9168	206.9168	206.9168
$J=1 \rightarrow 2$	413.8336	413.8336	413.8336	413.8336	413.8336	413.8336
$J=2 \rightarrow 3$	620.7504	620.7504	620.7504	620.7504	620.7504	620.7504
$J=3 \rightarrow 4$	827.6672	827.6672	827.6672	827.6672	827.6672	827.6672
$J=4 \rightarrow 5$	1034.5840	1034.5840	1034.5840	1034.5840	1034.5840	1034.5840
$J=5 \rightarrow 6$	1241.5008	1241.5008	1241.5008	1241.5008	1241.5008	1241.5008
$J=6 \rightarrow 7$	1448.4176	1448.4176	1448.4176	1448.4176	1448.4176	1448.4176
$J=7 \rightarrow 8$	1655.3344	1655.3344	1655.3344	1655.3344	1655.3344	1655.3344
$J=8 \rightarrow 9$	1862.2512	1862.2512	1862.2512	1862.2512	1862.2512	1862.2512
$J=9 \rightarrow 10$	2069.1680	2069.1680	2069.1680	2069.1680	2069.1680	2069.1680
$J=10 \rightarrow 11$	2276.0848	2276.0848	2276.0848	2276.0848	2276.0848	2276.0848
$J=11 \rightarrow 12$	2483.0016	2483.0016	2483.0016	2483.0016	2483.0016	2483.0016
$J=12 \rightarrow 13$	2689.9184	2689.9184	2689.9184	2689.9184	2689.9184	2689.9184
$J=13 \rightarrow 14$	2896.8352	2896.8352	2896.8352	2896.8352	2896.8352	2896.8352
$J=14 \rightarrow 15$	3103.7520	3103.7520	3103.7520	3103.7520	3103.7520	3103.7520
$J=15 \rightarrow 16$	3310.6688	3310.6688	3310.6688	3310.6688	3310.6688	3310.6688
$J=16 \rightarrow 17$	3517.5856	3517.5856	3517.5856	3517.5856	3517.5856	3517.5856
$J=17 \rightarrow 18$	3724.5024	3724.5024	3724.5024	3724.5024	3724.5024	3724.5024
$J=18 \rightarrow 19$	3931.4192	3931.4192	3931.4192	3931.4192	3931.4192	3931.4192
$J=19 \rightarrow 20$	4138.3360	4138.3360	4138.3360	4138.3360	4138.3360	4138.3360

### III. RESULTS

Because of the small moment of inertia of hydrogen cyanide, its rotational transitions fall in the millimeter and submillimeter region of the microwave spectrum. In this work, rotational transitions of  $\text{T}^{12}\text{C}^{14}\text{N}$ ,  $\text{T}^{13}\text{C}^{14}\text{N}$ , and  $\text{T}^{12}\text{C}^{15}\text{N}$  were observed in both the  $00^0$  and  $01^0$  vibrational states. In the ground vibrational state ( $00^0$ ) the transition frequencies of a linear molecule are given by

$$\nu = 2B_r(J+1) - 4D_r(J+1)^3. \quad (1)$$

In the first excited bending state ( $01^0$ ), the effects of  $l$ -type doubling must be included and the transition frequencies are given by (10)

$$\nu = 2B_r(J+1) \pm [q_2^{(0)} - q_2^{(1)}J(J+1)](J+1) - 4D_r(J+1)[(J+1)^2 - l^2], \quad (2)$$

where  $B_r$  and  $D_r$  have their usual meanings and  $q_2^{(0)}$  and  $q_2^{(1)}$  are the  $l$ -type doubling constant and the first correction to this constant due to centrifugal distortion respectively.

Hyperfine structure which results from the  $^{14}\text{N}$  nucleus is resolvable for both the  $J = 0 \rightarrow 1$  and  $J = 1 \rightarrow 2$  transitions and also produces small but observable shifts in the observed line frequencies of higher  $J$  transitions. Although quadrupole coupling constants can be calculated on the basis of the splittings observed in this work, beam maser measurements have shown that the difference in the nitrogen quadrupole coupling constant  $eqQ$  between HCN and DCN is very small (3). Since it would be expected that the difference between DCN and TCN would be even smaller, the value of  $eqQ$  was fixed at the DCN value of  $-4.7030$  MHz. The spin-rotation constant  $C_N$  of TCN can be calculated from the beam maser results of either HCN or DCN to be  $0.007$  MHz. This constant was also fixed in the analysis. This reduction in degrees of freedom in the

TABLE II. Observed and Calculated  $l$ -Type Doubling Constants (in  $\text{cm}^{-1}$ ).

Transition	$T^{12}C^{14}N$		$T^{13}C^{14}N$		$T^{12}C^{15}N$	
	$00^0_0$	$01^1_0$	$00^0_0$	$01^1_0$	$00^0_0$	$01^1_0$
$1 \leftarrow 0$	$214.412(1)^a$	$214.412(1)^a$	$214.412(1)^a$	$214.412(1)^a$	$214.412(1)^a$	$214.412(1)^a$
$2 \leftarrow 1$	$1.128(1)(1)$	$1.128(1)(1)$	$1.128(1)(1)$	$1.128(1)(1)$	$1.128(1)(1)$	$1.128(1)(1)$
$3 \leftarrow 2$		$1.128(1)(1)$		$1.128(1)(1)$		$1.128(1)(1)$
$4 \leftarrow 3$		$1.128(1)(1)$		$1.128(1)(1)$		$1.128(1)(1)$

a. The number in parentheses is number of observations.

least-squares analysis makes possible a somewhat more accurate calculation of the remaining constants.

In Table I are listed the measured transition frequencies of  $T^{12}C^{14}N$ ,  $T^{13}C^{14}N$ , and  $T^{12}C^{15}N$  in the  $00^0_0$  and  $01^1_0$  vibrational states. Also included in Table I are the differences between these observed frequencies and a set of transition frequencies calculated from the spectral constants of Table II.

Direct  $l$ -type doublet transitions have been observed in the centimeter region of the microwave spectrum for both  $H^{12}C^{14}N$  and  $D^{12}C^{14}N$  (5, 6). The  $l$ -type doubling constant  $q_2^{(0)}$  and its correction due to centrifugal distortion  $q_2^{(1)}$  have been calculated for each of these species from this spectra. Because of the spectral range, sensitivity, and resolution of the spectrometer described above, it is possible to calculate these constants for TCN directly from the observed millimeter and submillimeter rotational transitions shown in Table I. These constants are also included in Table II. Nielson and Shaffer (11) have shown that

$$q_2^{(0)} \propto B_e^2 \omega_e \quad (3)$$

Table III shows a comparison between the experimental values of  $q_2^{(0)}$  and those derived from Eq. (3) and the experimental value of  $q_2^{(0)}$  of  $T^{12}C^{14}N$ . This table shows that the agreement is about 0.07% for nonhydrogen substitution and about 1.0% for hydrogen substitution.

TABLE III. Observed and Calculated  $l$ -Type Doubling Constants (in  $\text{cm}^{-1}$ ).

Observed	Calculated	Calculated <sup>b</sup>
$q_2^{(0)}(T^{12}C^{14}N)$	$1.128(1)$	$1.128(1)$
$q_2^{(0)}(T^{13}C^{14}N)$	$1.128(1)$	$1.128(1)$
$q_2^{(0)}(T^{12}C^{15}N)$	$1.128(1)$	$1.128(1)$
$q_2^{(0)}(T^{12}C^{14}N)$	$1.128(1)$	$1.128(1)$
$q_2^{(0)}(T^{12}C^{14}N)$	$1.128(1)$	$1.128(1)$

a. The number in parentheses is number of observations.

Table IV. Comparison of Substitution and Equilibrium Structures for Hydrogen Cyanide.

Species				$r(\text{H-C}) \text{ \AA}$	$r(\text{C}\equiv\text{N}) \text{ \AA}$
$1, 12, 13$	$1, 12, 14$	$1, 13, 14$	$1, 12, 15$	1.0731	1.1553
$1, 13, 14$	$2, 12, 14$	$1, 13, 14$	$1, 13, 15$	1.0734	1.1553
$2, 12, 14$	$1, 12, 14$	$2, 13, 14$	$2, 12, 15$	1.0732	1.1550
$2, 12, 14$	$2, 12, 14$	$2, 13, 14$	$2, 12, 15$	1.0730	1.1550
$2, 12, 14$	$1, 12, 14$	$3, 13, 14$	$3, 12, 15$	1.0735	1.1549
$2, 12, 14$	$2, 12, 14$	$3, 13, 14$	$3, 12, 15$	1.0730	1.1549
Average				1.0730	1.1551
$\sigma$				0.0005	0.0002
Equilibrium <sup>12</sup>				1.0730	1.1550

a. Ref. 4.

#### IV. STRUCTURE

As a result of the strong rotation-vibration coupling in light, hydrogen-containing molecules, calculation of meaningful structures for these molecules is particularly difficult. For example, Winnewisser, Maki, and Johnson (4) have shown that the effective length  $r_o$  of the H-C bond varies by 0.02 Å when evaluated from various combinations of HCN and DCN isotopic species.

Costain has suggested that  $r_s$  (substitution) structures should be significantly more consistent than  $r_o$  (effective) structures and that they should also more closely approximate the  $r_e$  (equilibrium) structure (12). This work on the tritium species makes possible the calculation of a number of substitution structures. Table IV lists these structures for all possible isotopic combinations. Inspection of this table shows that the  $r_s$  structures are one to two orders of magnitude more consistent than the  $r_o$  structures calculated in Ref. (4) and that in addition they closely approximate the  $r_e$  structure. This is particularly true of the structures based on the heavier deuterium and tritium species. Since the vibrational effects, which are the limiting factors in structural determinations, are largest for hydrogen cyanide, it can be concluded that the substitutional structures of other linear molecules should be equally consistent and in good agreement with the equilibrium structure.

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