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Millimeter-wave laboratory detection of $HNCCN^+$

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The ground-state rotational spectrum of protonated cyanogen, $HNCCN^+$, has been identified following the infrared detection by Warner and Amano [J. Mol. Spectrosc. **145**, 66 (1991)], using a hollow cathode discharge as production source. The rotational and centrifugal distortion constants have been determined to be 4438.010 13(71) MHz and 0.529 95(24) kHz, respectively.

I. INTRODUCTION

CN was one of the first molecular species found in interstellar space in 1937 by optical absorption against stars.[1] Subsequently, a famous observation by McKellar[2] indicated that the excitation temperature of CN is 2.7 K. More recently radio astronomical observations have led to the discovery of several cyanocompounds including the famous cyanopolyynes, $HC_{2n+1}N$ ($n = 1$–5), in various interstellar objects, such as molecular clouds, circumstellar envelopes, and star forming regions.[3] Yet, no molecule containing two or more CN groups has been discovered in interstellar space. The simplest molecules with two CN groups, all linear molecules, are cyanogen (NCCN), isocyanogen (CNCN), and diisocyanogen (CNNC).

Among the different spectroscopic methods to search for molecules in space, certainly the radio detection of rotational transitions is the most selective and sensitive one. Unfortunately, both cyanogen and diisocyanogen are centrosymmetric and, therefore, not detectable by their rotational spectrum. On the other hand, CNCN has an electric dipole moment of 0.68 D and its laboratory microwave spectrum has been observed, together with the infrared and far-infrared spectra.[4] Recently, Warner and Amano[5] succeeded in observing the ν_1 and $\nu_1 + \nu_7 - \nu_7$ bands of $HNCCN^+$ with a difference frequency laser spectrometer and a hollow cathode discharge. This ion has a linear structure and a calculated dipole moment of 6.4 – 6.8 D (Refs. 6 and 7) and is therefore an interesting candidate for observation. In view of this possibility we undertook the search of its ground-state rotational spectrum in the millimeter-wave region using a hollow cathode discharge as the production source.

II. EXPERIMENTAL DETAILS

The detailed description of the millimeter-wave spectrometer and of the hollow cathode discharge has already been given elsewhere.[8] Here only a brief account will be outlined. The millimeter-wave radiation is obtained by harmonic generation from a phase-locked Gunn oscillator, which oscillates in the frequency region 80–110 GHz with 30 mW power. We used a Schottky barrier diode mounted in a commercial multiplier (Millitech). Tone burst modulation was employed following the scheme of Pickett.[9] The tone frequency was set at 1 MHz and it was switched at 40 kHz. The signal was phase sensitively detected at the switching frequency. The microwave power transmitted through the hollow cathode cell was detected by an InSb hot electron detector operated at liquid-helium temperature. Data acquisition, frequency scanning, and line frequency measurements are processed on line by a microcomputer system.

As for other short-lived species studied in this laboratory,[8] the $HNCCN^+$ ion is produced inside a hollow cathode discharge run at a dc current of about 500 mA. The $HNCCN^+$ lines turned out to be very sensitive to both pressure and temperature conditions. The best results have been obtained by flowing through the cell a mixture of 1 mTorr NCCN taken from a commercial cylinder (Matheson) without further purification and 25 mTorr H_2 (1 mTorr = 0.133 Pa). A mechanical booster pump and a liquid-nitrogen trap were used to keep the flow rate as high as possible. Circulation of cooled methanol at − 60 °C was maintained through a copper tubing soldered onto the outer surface of the cathode to lower the rotational temperature and, possibly, the diffusion loss.

Line frequencies were predicted using the rotational constants derived in Ref. 5. A magnetic field of about 70 G, applied to the hollow cathode, allowed us to discriminate between ions and neutrals when desired.

III. RESULTS AND DISCUSSION

The lines have been measured in the range from 248 to 373 GHz, and their frequencies are listed in Table I. The largest deviation from the frequencies calculated using the

TABLE I. Rotational transitions of $HNCCN^+$ in the ground state (in MHz).

J'	J''	Obs.	Δ^a
28	27	248 482.034	1
30	29	266 223.393	20
31	30	275 093.490	13
32	31	283 962.857	− 330[b]
37	36	328 305.311	− 65
38	37	337 172.436	− 16
39	38	346 039.038	− 8
40	39	354 905.187	44
41	40	363 770.758	26
42	41	372 635.788	− 11

[a] (Obs.-Calc.) × 10^3.
[b] Not included in the fit. The measured frequency is affected by an interfering line.

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infrared data[5] turned out to be 6 MHz. Transition frequencies were measured by averaging three independent up- and down-scan measurements, respectively. Frequencies are believed to be accurate to $\pm$ 30 kHz.

Figure 1(a) is a typical 10 MHz tracing after 150 scans, and it shows the $J = 39 \leftarrow 38$ ground-state line of $HNCCN^+$ at 346 039.038 MHz. The conditions are those already described in Sec. II, that is, 1 mTorr NCCN is mixed with 25 mTorr H_2. By increasing the NCCN pressure to 2 mTorr, the line disappears and, as seen in Fig. 1(b), another line shows up very close by. This accident caused an initial misassignment of the whole spectrum.

The fitted spectroscopic constants are presented in Table II together with those previously obtained from the infrared analysis[5] and coupled-electron-pair-approximation (CEPA) calculations.[7] The present rotational constant B_0 agrees within three standard errors with that obtained from the infrared analysis, while the centrifugal distortion constant D_0 is definitely out of this error range. Its value is now very close to the theoretical one. The accuracy of the parameters determined in this work, B_0 and D_0, is improved by 2 orders of magnitude compared to that in the previous infrared work.[5]

Raksit and Bohme[10] studied the reaction

$$H_3^+ + C_2N_2 \rightarrow H_2 + HNCCN^+ \qquad (1)$$

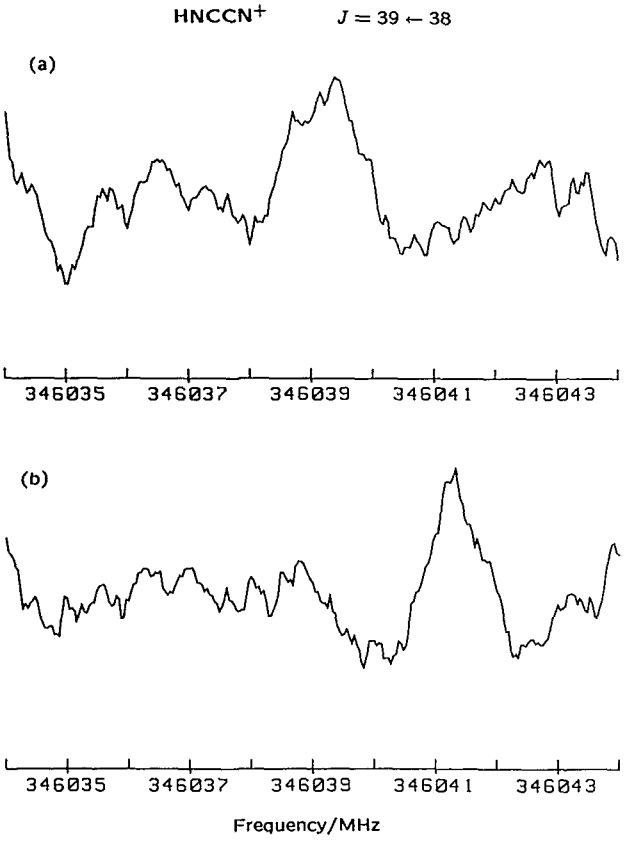

FIG. 1. A 10 MHz tracing after 150 scans at two different NCCN pressures and at constant 25 mTorr H_2. (a) The line corresponding to the $J = 39 \leftarrow 38$ transition of $HNCCN^+$ appears at 346 039.038 MHz when 1 mTorr NCCN and 25 mTorr H_2 are flowed through the hollow cathode. (b) Varying only the pressure of NCCN to 2 mTorr the previous line disappears, while an unknown line shows up very close by.

TABLE II. Fitted spectroscopic constants from the ground-state rotational spectrum of $HNCCN^+$ and comparison with previous works.

	Present work	IR work[a]	Theoretical[b]
B_0/MHz	4438.010 13(71)[c]	4438.23(8)	4435
D_0/kHz	0.529 95(24)	0.602(25)	0.493

[a] Reference 5.
[b] Reference 7.
[c] The values in parentheses denote on standard error in units of the last digit in the constant.

to determine the proton affinity of C_2N_2. In their flow tube experiments, the abundance of $HNCCN^+$ reached a plateau at relatively low C_2N_2 flow rate and stayed at that level with increasing flow rate of C_2N_2 (see Fig. 2 of Ref. 10). However, under our laboratory conditions in a hollow cathode discharge, we have found that the yield is rather poor, because of a great many alternative reactions, leading to products other than $HNCCN^+$. In fact, we have observed lines of various other species, such as CN, HCN, HNC, HC_3N, CH_3CN, and CH_2CHCN. As the proton affinities of these species, except for CN (the proton affinity of CN is not known), are larger than that for C_2N_2,[11] the sharp decrease of $HNCCN^+$ observed when the pressure of C_2N_2 was increased to 2 mTorr from 1 mTorr may be explained by the proton transfer reactions from $HNCCN^+$ to those molecules. Another likely reason for a low abundance of $HNCCN^+$ in our laboratory conditions is the probable very fast dissociative recombination of $HNCCN^+$ with electrons.

A variety of cyanocompounds has been discovered in interstellar space. All of them contain only one CN group. To entrain another CN group, reactions between two or more cyanocompounds should take place. Reactions leading to the formation of C_2N_2 such as

$$C_2N^+ + CH_3CN \rightarrow C_2H_3^+ + C_2N_2, \qquad (2)$$

$$C_2N^+ + HC_3N \rightarrow C_3H^+ + C_2N_2, \qquad (3)$$

have been studied in the laboratory.[12] All these reactions proceed with Langevin or near Langevin rate. Stroh and Winnewisser[4] have, in fact, proposed a similar mechanism to form CNCN in the interstellar medium. Then $HNCCN^+$ will likely be formed by proton transfer reactions in addition to the reaction (1)

$$HX^+ + C_2N_2 \rightarrow HNCCN^+ + X, \qquad (4)$$

where X = CO, N_2, C_2H_2, OH, for example, and will be depleted by the dissociative recombination with electrons and the proton transfer reactions

$$HNCCN^+ + Y \rightarrow C_2N_2 + HY^+, \qquad (5)$$

where Y = C_2H_4, CH_3OH, H_2O, for example, resulting in recycling C_2N_2 back to the system.

The detection of CNCN and/or $HNCCN^+$ in space, for both of which microwave data are now available, would affect the reaction models of interstellar chemistry. So far these models do not contain any molecular species with more than one CN group.

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