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Submillimeter-wave rotational spectra of DNC in highly excited vibrational states observed in an extended negative glow discharge

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ABSTRACT

Rotational transitions of DNC have been observed in the submillimeter-wave region in an extended negative glow discharge in a gas mixture of CD_4 and N_2. The dissociative recombination reaction of $DCND^+$ with electrons is thought to be a dominant channel to produce DNC in highly excited vibrational states. The vibrational temperature for the ν_3 vibrational mode is found to be about 4000 K, and the rotational lines in levels up to (008) are observed. The rotational and centrifugal distortion constants are determined for these states along with those for the (100) state. The measurement accuracy is high enough to determine some higher order vibration–rotation interaction constants.

1. Introduction

Spectroscopic investigations of DNC have been less extensive than those for HNC. Nevertheless, as early as in 1976, the first laboratory identification of rotational lines of DNC was made by Creswell et al. [1] and Blackman et al. [2]. Shortly after that, the $J = 1 - 0$ and the $J = 2 - 1$ lines were detected toward several interstellar molecular sources [3,4], and revealed much higher abundances of the D-species than had been expected from the cosmic abundance ratio. Okabayashi and Tanimoto [5] observed the rotational lines of HNC/DNC in all three fundamental excited vibrational states by using a glow discharge in the laboratory, and the equilibrium molecular structure was determined. More recently, Brünken et al. extended the measurements of the rotational lines up to 2 THz in the ground state and the first excited state of the bending vibration [6], and obtained the improved molecular constants for these states. Bechtel et al. [7] employed a discharge nozzle source combined with millimeter-wave radiation sources to observe the $J = 1 - 0$, $J = 2 - 1$, and $J = 3 - 2$ lines for HNC and DNC, and the electric quadruple hyperfine structures were investigated. Due to the jet expansion technique they used, the accuracy of the frequency measurements for these transitions were greatly improved.

Extended negative glow discharge in a gas mixture of CH_4 and N_2 is known to be a very good source of $HCNH^+$ [8,9], and the dissociative recombination of $HCNH^+$ with electrons is a major pathway to form HNC in a discharge. This is also a process leading to formation of HNC in interstellar molecular clouds. In dark clouds, HNC is by far more abundant than is expected from thermochemical equilibrium. In dense molecular clouds, HCN and HNC are produced predominantly through the dissociative recombination reactions,

$$HCNH^+ + e^- \rightarrow HCN + H \quad (1)$$

$$\rightarrow HNC + H. \quad (2)$$

To explain the high abundance of HNC, the branching ratio to yield HCN and HNC is thought to be approximately unity, as has been extensively investigated theoretically (see for example [10–15] and references cited therein). Experimental determination of the branching ratio is difficult. Semaniak et al. [16] investigated the branching ratio by using an ion storage ring. However, because they used mass spectrometric detection, the ratio which yields HCN and HNC was not separately determined. We presented a laboratory measurement of the branching ratio made by using a characteristic behavior of formation of HCN/HNC and DCN/DNC in an extended negative glow discharge [17].

While investigating the [DCN]/[DNC] abundance ratio, it was found that the vibrational temperature for the ν_3 mode of DNC was very high, reaching as high as 4000 K. In this investigation, the rotational transitions in the ν_3 excited vibrational states up to (008) will be reported, in addition to extension of the measurements of the lines in the (100) state.

2. Experimental procedure and the results

Submillimeter-wave lines of DNC were observed with a BWO(Backward-wave Oscillator) based spectrometer system [18,19]. A gas mixture of 15 mTorr of N_2 and 1–2 mTorr of CD_4 was flowed through a liquid nitrogen cooled discharge cell with the optimum discharge current set at about 18 mA. Cooling the discharge cell down to liquid nitrogen temperature was a very important factor to see rotational lines in highly excited vibrational

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states. Fig. 1 shows examples of the rotational lines in the excited v_3 states. A line in the (100) state is also shown for comparison. The relative intensities in these panels are hard to compare quantitatively, because the radiation power was not normalized and the spectra were recorded with different conditions such as gain settings of the amplifiers and integration time. The Boltzmann plot given in our previous paper [17] should provide a better indication of about the relative intensity.

Least-squares fits were performed for each individual vibrational state. For low-v_3 states, a higher order centrifugal distortion constant H was determined. For high-v_3 states, however, it was marginal, so the H term was not included in the fits. Table 1 summarizes the rotational lines measured and the results of the least-squares fits. The rotational lines for (001) measured by Okabayashi and Tanimoto [5] were also included in the fit, and they agreed well within their estimated uncertainties. The fits for the (004), (006), and (008) states were not as good as for the other states, so the results for these states are listed separately in Table 2. Table 3 lists the measured lines and the results of the fit for the (100) state. The fitted parameters for ($00v_3$) are listed in Table 4. The rotational and centrifugal distortion constants determined by Okabayashi and Tanimoto [5] for the (100) state agree very well, but the centrifugal distortion constant for the (001) state differs beyond the quoted uncertainty.

The deviations of the fits for (004), (006), and (008) are definitely larger than the experimental uncertainties that range from 10 to 60 kHz, as shown in the columns (o–c) I of Table 2. Fig. 2 shows the vibrational dependence of the centrifugal distortion constants. The deviations of the centrifugal distortion constants for (004), (006), and (008) states are clearly seen in Fig. 2a. An enlarged figure obtained by eliminating the data points corresponding to (004), (006), and (008) is shown in Fig. 2b. A fitted curve obtained by fitting to the second order polynomials is also shown. The results of the fits obtained by fixing the centrifugal distortion constants at the values for these states interpolated by using this fitted curve in Fig. 2b are listed in the column (o–c) II of Table 2. We hoped that this process might reveal systematic deviations, but it was not obvious except for the (006) state.

This anomaly also affects the rotational constants as indicated in Table 4; the errors of B for these states are definitely larger compared with those for other states. Fig. 3 shows the v_3 dependence of the difference of the rotational constants, $\Delta B_{v-1,v} = B_{v-1} - B_v$. On this frequency scale, the deviations of the rotational constants are not discernible.

Figs. 2 and 3 demonstrate that the measurement accuracy is high enough to derive some information of higher-order vibration–rotation constants. The vibrational dependence of the rotational constants is given by

$$B(v_1, v_2, v_3) = B_e - \sum_i \alpha_i(v_i + d_i/2) + \sum_{i\leqslant j} \gamma_{ij}(v_i + d_i/2)(v_j + d_j/2) + \sum_{i\leqslant j\leqslant k} \delta_{ijk}(v_i + d_i/2)(v_j + d_j/2)(v_k + d_k/2) + \cdots \quad (3)$$

More specifically the rotational constant for the ($00v_3$) states is expressed, by ignoring the higher-order terms, as

$$B(0,0,v_3) = (B_e - \alpha_1/2 - \alpha_2 + \gamma_{11}/4 + \gamma_{22} + \gamma_{12}/2 + \delta_{111}/8 + \delta_{222} + \delta_{112}/4 + \delta_{122}/2) - (\alpha_3 - \gamma_{13}/2 - \gamma_{23} - \delta_{123}/2 - \delta_{223})(v_3 + 1/2) + (\gamma_{33} + \delta_{133}/2 + \delta_{233})(v_3 + 1/2)^2 + \delta_{333}(v_3 + 1/2)^3. \quad (4)$$

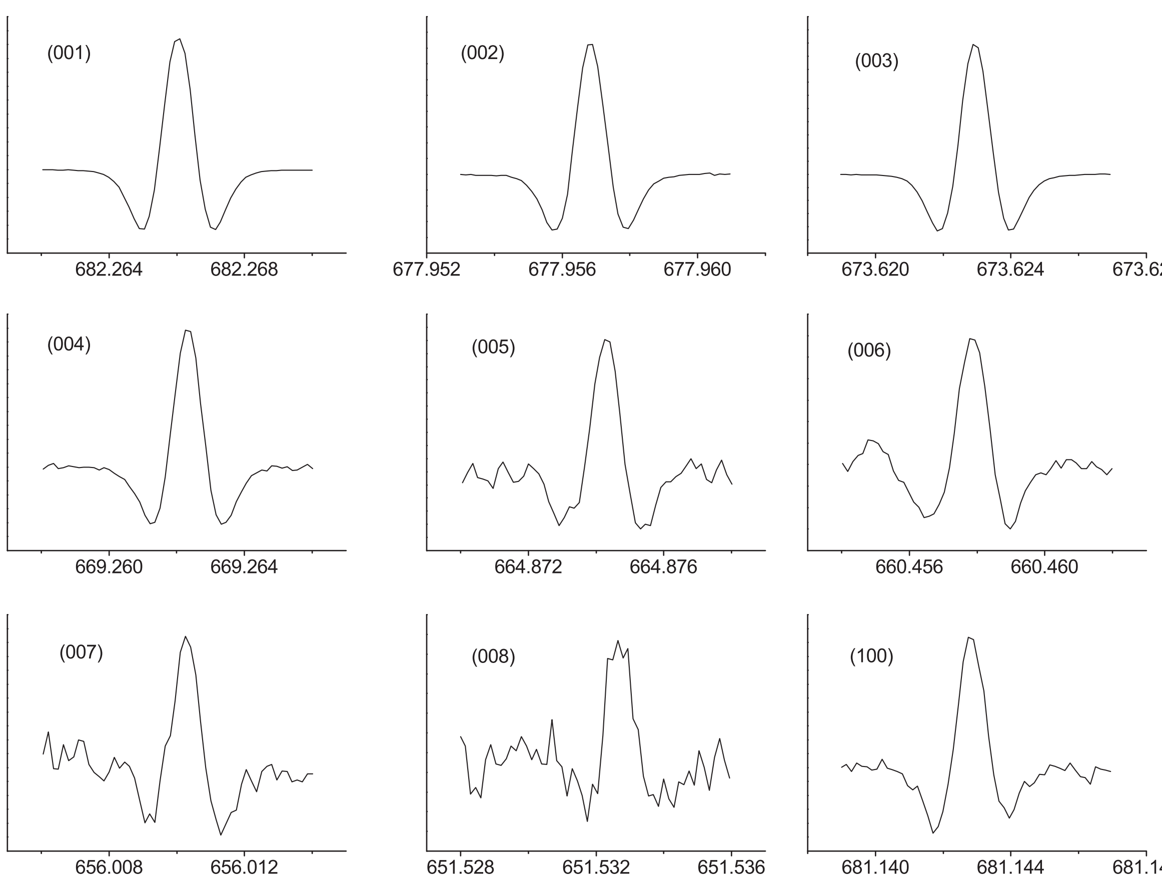

Fig. 1. Overview of the $J = 9 - 8$ lines in the excited vibrational states. The frequency scale for all the panels is in the GHz units. The line in the (100) state is also shown for comparison. The relative intensities in these panels are hard to compare becuase the radiation power was not normalized and the spectra were recorded with different conditions such as the total accumulation time. The Boltzmann plot was shown in our previous paper [17].