

*Letter to the Editor***The submillimeter-wave spectrum of hydrogenisocyanide, HNC, in its (0, 0, 0) and (0, 1, 0) vibrational states up to 2 THz**

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**Abstract.** The submillimeter-wave spectrum of hydrogenisocyanide, HNC, in its ground vibrational (0, 0, 0) and first excited bending states (0, 1, 0) (vibrational states are denoted  $(v_1, v_2, v_3)$ ) has been measured from 453 to 1991 GHz spanning the rotational quantum numbers  $5 \leq J_u \leq 22$ . The new transition frequencies were fitted together with previously published data, providing a comprehensive set of molecular parameters up to sextic centrifugal distortion constants. The present data set allows for the prediction of accurate rest frequencies well beyond 2 THz.

**Key words:** molecular data – methods: laboratory – techniques: spectroscopic – ISM: clouds – ISM: molecules – radio lines: ISM

**1. Introduction**

In 1971, the observation of a new interstellar line at  $90665 \pm 1$  MHz (U90.7) was reported by Snyder and Buhl (1971, 1972). By structural considerations (estimation of the rotational constant  $B$ ), this line was attributed to HNC, a molecule that had been observed previously only by means of matrix-isolation spectroscopy in the laboratory (Milligan and Jacox 1963, 1967). Shortly thereafter, Zuckerman et al. (1972) derived an improved value of  $90663.9 \pm 0.5$  MHz for its rest frequency from observations of the young cluster NGC 2264. The first millimeter-wave investigations to confirm this tentative assignment were performed by Blackman et al., Creswell et al., and Saykally et al. in 1976. Since these early days, only one additional work on the pure rotational spectrum of HNC up to  $J = 4 - 3$  has been reported by Okabayashi and Tanimoto (1993). The authors detected rotational transitions of the molecule in its (0, 0, 0), (1, 0, 0), (0, 1, 0), and (0, 0, 1) vibrational states.

The isomeric pair HCN/HNC is of enormous astrophysical interest (e.g. Schilke et al. 1992, Turner et al. 1997, Hirota et al. 1998, Talbi and Herbst 1998, Herbst et al. 2000), but the laboratory data available on HNC is by far not as extensive as the data on HCN. Very recently, Maiwald et al. (2000) reported

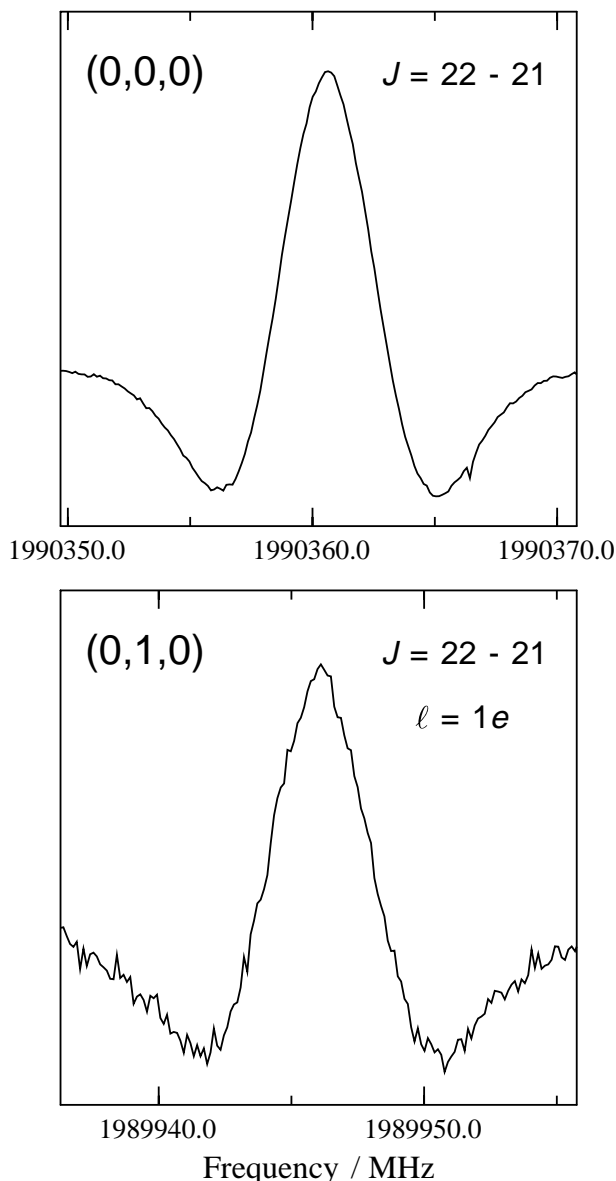
on the submm-wave spectrum of HCN up to 1.95 THz whereas for HNC 365 GHz marks the upper limit (Okabayashi and Tanimoto 1993). The pure rotational spectrum of HNC in its ground vibrational state has been observed in the protoplanetary nebula CRL 618 by Herpin and Cernicharo (2000) up to  $J = 22 - 21$ , which corresponds to a frequency of approximately 2 THz, using the Infrared Space Observatory, ISO. This very transition has been measured in the laboratory in the present study (see Table 1 and Fig. 1). The rotational energy of the  $J = 22 - 21$  ground state transition of HNC is about  $698 \text{ cm}^{-1}$  (1005 K) and therefore significantly higher than the energy of  $464 \text{ cm}^{-1}$  for the bending fundamental. In comparison, the fundamental bending mode of HCN lies at  $712 \text{ cm}^{-1}$ . Nevertheless, features due to this and even higher vibrational states have been detected in astronomical sources (e.g. Ziurys and Turner 1986, Schilke et al. 2000). This indicates, that it could be possible to detect vibrational satellites of HNC in warmer regions of the interstellar and circumstellar medium provided it can survive radiative penetration.

Further extension of the frequency range up to the far infrared (THz range) by laboratory spectroscopy is required by future missions such as SOFIA (Stratospheric Observatory For Infrared Astronomy) and FIRST (Far InfraRed and Submillimetre Telescope) to unambiguously identify the carriers of spectral features and to allow for proper kinematical analyses.

In this Letter, we report the investigation of pure rotational transitions of HNC in its (0, 0, 0) and (0, 1, 0) states up to 2 THz.

**2. Experimental**

HNC was synthesized *in situ* in a flow system *via* dc glow discharge of 2–10 Pa methyl cyanide,  $\text{CH}_3\text{CN}$ , and up to 20 Pa Helium. Two different spectrometers were employed: In the lower submm-range ( $< 913$  GHz), the Cologne terahertz spectrometer (Winnewisser et al. 1994, Winnewisser 1995) was used with its phase-stabilized backward-wave oscillators (ISTOK Research and Production Company, Moscow region, Russia) (Lewen et al. 1998) as sources. Measurements near two terahertz were carried out using the Cologne sideband spectrometer for terahertz applications (COSSTA) (Gendriesch et al. 2000) employing a double modulation technique: modulating the dis-



**Fig. 1.** Examples of HNC spectra recorded close to two terahertz. The upper trace shows the  $J = 22 - 21$  ground state transition at 1990360 MHz and the lower its  $\ell = 1e$  vibrational satellite at 1989846 MHz.

charge by 11 Hz and the source frequency by 27 kHz. Two different absorption cells of 2 and 1 m length, respectively, were used. Magnetically tuned, liquid-He-cooled InSb hot electron bolometers were employed as detectors.

### 3. Analysis and discussion

The energy expression for a linear molecule in its ground vibrational state is given by

$$E_{0,J} = B_0[J(J+1)] - D_0[J(J+1)]^2 + H_0[J(J+1)]^3. \quad (1)$$

Bending modes in linear molecules are doubly degenerate since the molecule is free to bend in two orthogonal planes. If

**Table 1.** Ground state and first excited bending state assignments, frequencies (MHz)<sup>a</sup>, and residuals  $o-c$  (kHz) of HNC

| $J' \leftarrow J''$ | $v^b$ | $\ell$ | frequency          | $o-c$ |
|---------------------|-------|--------|--------------------|-------|
| 5 $\leftarrow$ 4    | 0     | 0e     | 453 269.922 (20)   | -9    |
| 5 $\leftarrow$ 4    | 1     | 1e     | 453 175.026 (30)   | 18    |
| 5 $\leftarrow$ 4    | 1     | 1f     | 456 415.184 (30)   | 14    |
| 6 $\leftarrow$ 5    | 0     | 0e     | 543 897.554 (15)   | -13   |
| 6 $\leftarrow$ 5    | 1     | 1e     | 543 783.709 (20)   | 10    |
| 6 $\leftarrow$ 5    | 1     | 1f     | 547 670.061 (30)   | 25    |
| 8 $\leftarrow$ 7    | 0     | 0e     | 725 107.341 (10)   | 9     |
| 8 $\leftarrow$ 7    | 1     | 1e     | 724 955.650 (20)   | 12    |
| 8 $\leftarrow$ 7    | 1     | 1f     | 730 131.117 (20)   | -14   |
| 9 $\leftarrow$ 8    | 0     | 0e     | 815 684.676 (10)   | 1     |
| 9 $\leftarrow$ 8    | 1     | 1e     | 815 514.083 (20)   | -22   |
| 9 $\leftarrow$ 8    | 1     | 1f     | 821 332.280 (20)   | 33    |
| 10 $\leftarrow$ 9   | 0     | 0e     | 906 240.459 (15)   | -12   |
| 10 $\leftarrow$ 9   | 1     | 1e     | 906 051.043 (50)   | -5    |
| 10 $\leftarrow$ 9   | 1     | 1f     | 912 510.238 (80)   | -99   |
| 21 $\leftarrow$ 20  | 1     | 1e     | 1 899 853.637 (60) | -4    |
| 21 $\leftarrow$ 20  | 1     | 1f     | 1 913 221.605 (75) | -37   |
| 22 $\leftarrow$ 21  | 0     | 0e     | 1 990 360.608 (50) | -7    |
| 22 $\leftarrow$ 21  | 1     | 1e     | 1 989 946.077 (75) | 62    |

<sup>a</sup> Uncertainties are given in parentheses in units of the least significant digits.

<sup>b</sup> 0 indicates the (0, 0, 0) and 1 the (0, 1, 0) vibrational state.

the molecule is bending and rotating simultaneously, the degeneracy is lifted giving rise to a phenomenon denoted *l-type doubling*: The bending state can be regarded as having components of an additional angular momentum  $p = \ell\hbar$  about the internuclear axis with  $\ell = v, v-2, v-4, \dots, -v$ . Hence, for a first excited bending mode  $\ell = +1, -1$  causes the splitting of every rotational level into two sublevels. Within these substates (either 1e or 1f, according to the notation of Brown et al. 1975) transitions with  $\Delta J = \pm 1$  can be observed. Thus, each ground state transition is accompanied by two further transitions for each first excited bending state. These considerations lead to an energy expression for the ground state transitions and the so-called *vibrational satellites* of the (0, 1, 0) state that is given by

$$E_{v,J} = B_v[J(J+1) - \ell^2] - D_v[J(J+1) - \ell^2]^2 + H_v[J(J+1) - \ell^2]^3 \pm \frac{1}{2}[q + q_J J(J+1) + q_{JJ}[J(J+1)]^2]J(J+1), \quad (2)$$

with  $q$  being the  $\ell$ -type doubling constant and  $q_J$  and  $q_{JJ}$  being its centrifugal distortion corrections. For the ground vibrational state  $\ell^2$  is zero and for the first excited bending mode  $\ell^2$  is one.

The spectra of two lines near two terahertz are shown as examples in Fig. 1. The list of experimental transition frequencies obtained in the present investigation is given in Table 1. The analysis has been performed fitting both states simultaneously using Pickett's program SPFIT (1991) under consideration of previously reported rovibrational data of the (0, 1, 0)  $\leftarrow$  (0, 0, 0) band by Burkholder et al. (1987), the very

**Table 2.** Molecular Parameters (MHz) of HNC

| Parameter             | (0,0,0)             | (0, 1, 0)          |
|-----------------------|---------------------|--------------------|
| $B_v$                 | 45 331.984 25 (113) | 45 484.461 95 (95) |
| $D_v \times 10^3$     | 99.828 9 (86)       | 103.194 7 (75)     |
| $H_v \times 10^9$     | 168.7 (104)         | 176.7 (96)         |
| $q_2$                 |                     | 324.368 6 (17)     |
| $q_{2J} \times 10^3$  |                     | -7.057 (12)        |
| $q_{2JJ} \times 10^9$ |                     | 242. (14)          |
| $\Delta E$            | 13 872 068.8 (12)   |                    |
| wrms <sup>a</sup>     | 0.89                |                    |

<sup>a</sup> Weighted rms.

recent data by Maki and Mellau (submitted), and the pure rotational transitions given in Okabayashi and Tanimoto (1993). Sextic centrifugal distortion constants could be determined for both states. The complete set of molecular parameters obtained is shown in Table 2.

The present data allows for prediction of accurate transition frequencies far beyond 2 THz. All data related to the results presented here (complete line list, fit file etc.) can be found online in the Cologne Database for Molecular Spectroscopy (CDMS) through <http://www.ph1.uni-koeln.de/vorhersagen/daten/>. Predictions of the pure rotational spectrum for both states presented here are available online from the CDMS via <http://www.ph1.uni-koeln.de/vorhersagen/catalog/>. Generally, the CDMS is accessible free of charge through <http://www.ph1.uni-koeln.de/vorhersagen/> or via its shortcut <http://www.cdms.de/>.

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