# High Resolution Spectrum of the $CH_3NC$ $\nu_2$ Fundamental Band [1]

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Z. Naturforsch. **44a**, 507–512 (1989); received March 10, 1989

The spectrum of methyl isocyanide ($CH_3NC$) has been measured in the region from 2148 $cm^{-1}$ to 2179 $cm^{-1}$ using a tunable diode laser spectrometer employing a newly designed signal averaging technique. The P-, Q- and R-branch lines of the $\nu_2$ fundamental band have been assigned for values of $J \leq 25$, $K \leq 12$. Molecular constants for the $\nu_2$ state have been determined including the quartic centrifugal distortion parameters.

## Introduction

Methyl isocyanide is the simplest isocyanide which is stable under laboratory conditions, and is spectroscopically of interest as a reference molecule for many other stable and unstable isocyanides. For the ground vibrational state the molecular constants are known very accurately. Several low lying vibrational states have been studied in detail from their microwave spectra [1]. However for the high energy state $\upsilon_2 = 1$ (2166 $cm^{-1}$) the spectroscopic knowledge is scarce. Low resolution spectra of the $CH_3NC$ fundamental bands were reported by several authors, e.g. Thompson and Williams [2], Williams [3], Thomas, Leisegang, and Thompson [4]. These spectra, however, lack the resolution required to extract from them reliable upper state molecular constants.

Inspection of the ground state centrifugal distortion constants, in particular $D_{JK} = 7.56 \cdot 10^{-6}$ $cm^{-1}$, reveals that the expected $K$-structure which accompanies each $J$ transition in the $\nu_2$ band is very tight and can only be resolved by high resolution spectroscopy. Consequently the low resolution work stands no chance to resolve the important $K$-structure. In addition the $\nu_2$ band is confused by at least two overlapping hot bands of the $\nu_8$ bending mode. Thus only few transitions were assigned from the low resolution spectrum, leading to an approximate band center determination and $B' - B''$.

In the present work the $\nu_2$ band, i.e. the $N$-$C$ stretching mode, of $CH_3NC$ was recorded with Doppler limited tunable diode laser (TDL) spectroscopy in the region between 2148 $cm^{-1}$ and 2179 $cm^{-1}$. The rotational $K$-structure of the individual $J$ transitions of the $\nu_2$ vibration has been resolved. Consequently, the molecular constants of the $\nu_2$ state have been determined completely by fixing the ground state constants to values obtained by a microwave study of Gondon [5].

## Experimental

The $CH_3NC$ sample was prepared by the reaction of N-methyl-formamide with a solution of p-toluenesulfochloride (toluene-p-sulphonyl chloride) in Quinoline [6].

The spectrum was recorded using a conventional TDL spectrometer from Laser Analytics, Model LS-3. For data processing, a computer controlled signal averager, which was originally developed in our laboratory for the data acquisition of the acousto optical spectrometers [7] used for interstellar spectroscopy, was redesigned for the needs of TDL spectroscopy. Here the spectroscopic data are stored in 2048 channels. Every 4.4 μs the detector signal is digitized and added to the value of the corresponding channel in the averager's storage unit. Then the diode current is increased by a channel fraction of a scan of typically 0.5 $cm^{-1}$. In about 9 ms a complete scan is recorded, and after a deadtime of 1 ms a new scan is started.

To maintain the spectral resolution while averaging, the thermal drifts of the laser control electronics (Laser Analytics LCM, CTS) must be sufficiently low. In the fast scan mode the width of the etalon fringes, which is typically 70 MHz, was observed to be broadened at a rate of 230 kHz for 1 min averaging. This is surprisingly stable comparing with the 10 MHz long

[1] This work was supported in part by the Deutsche Forschungsgemeinschaft, SFB-301.

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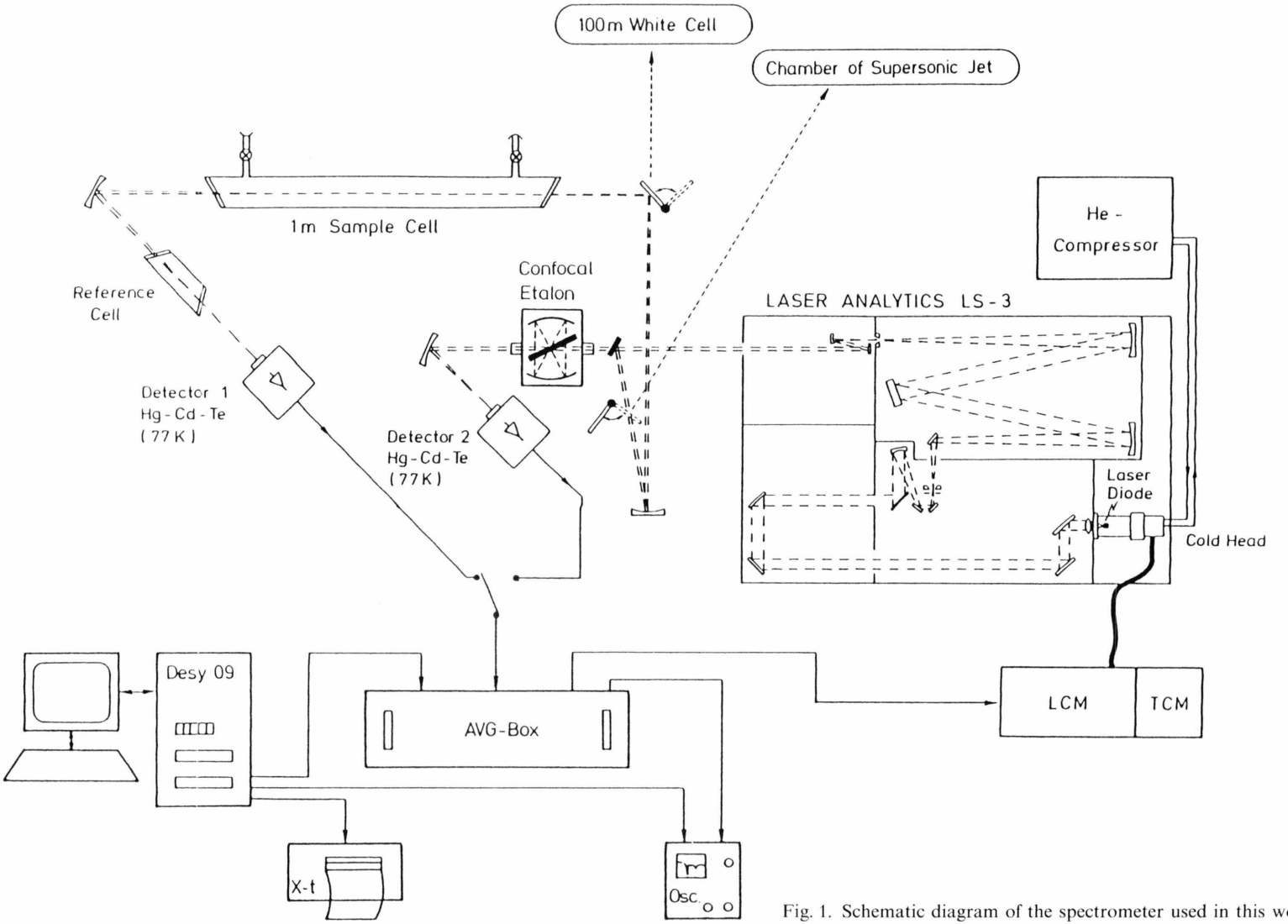


Fig. 1. Schematic diagram of the spectrometer used in this work

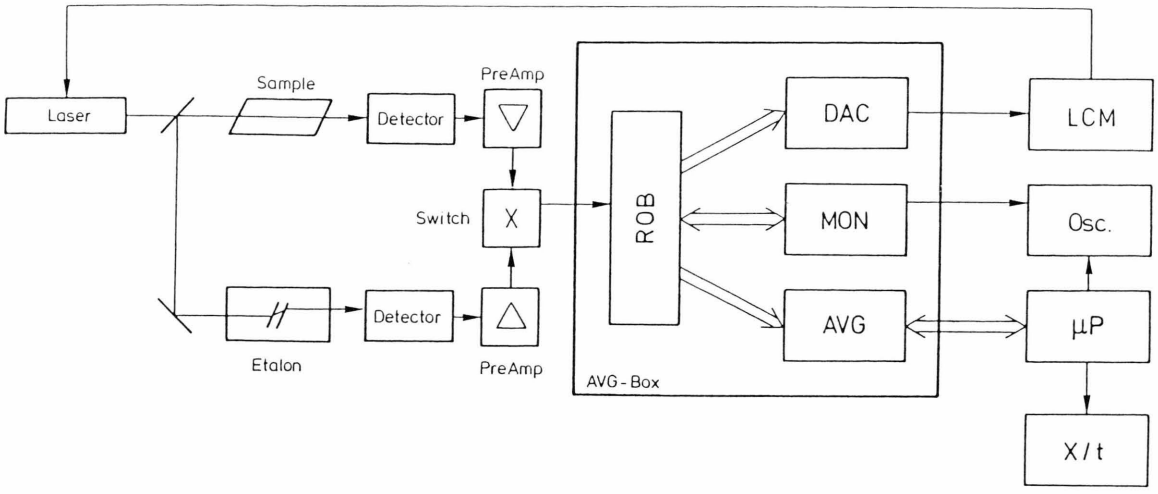


Fig. 2. Schematic picture showing the data processing system in detail. The readout board (ROB) digitizes the detector signals and transfers them to the averager (AVG). All timing control signals are produced by the ROB. The Monitor board (MON) interfaces between the system and monitoring instruments like oscilloscops (OSC). Using a D/A converter (DAC), a saw-tooth signal is generated to scan the laser frequency parallel to the processing timing. After integration the averager data are submitted to a microcomputer (µP) to save them on floppy disk.

term thermal drift which was measured for a TDL spectrometer without scanning [8]. Under the present conditions integration times of several minutes could be achieved, and consequently averaging over tens of thousands scans was possible.

As a relative frequency scale a confocal Fabry-Perot interferometer (FPI) was used, which was constructed in our laboratory [9] with a free spectral range of about 0.01 $cm^{-1}$. Absolute frequencies were obtained by using NNO as a reference gas (see Figure 1). In this range the NNO line frequencies are known with an accuracy of around $10^{-4}$ $cm^{-1}$ [10]. Spectra of the sample gas, of FPI, and of the calibration gas were measured sequentially. The spectra were stored on the floppy disk of a dedicated laboratory computer and were then transferred for further analysis to a Micro VAX II computer. With the help of FORTRAN programs, line positions were found and calibrated with an accuracy of $3 \cdot 10^{-4}$ $cm^{-1}$.

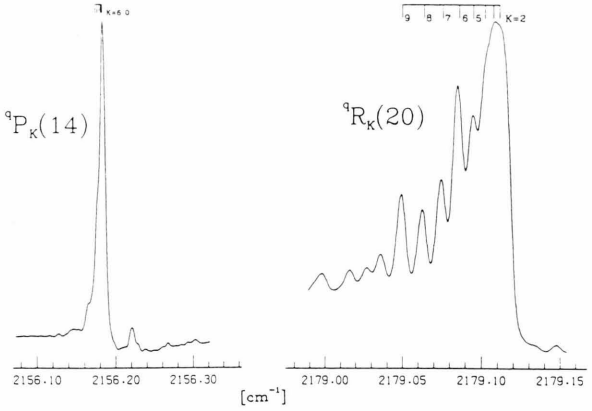


Fig. 3. Part of the observed spectrum showing $^qP_K$ (14) and $^qR_K$ (20).

## Assignment and Calculations

The energy levels of a prolate symmetric top molecule like $CH_3NC$ are given by

$$F(v, J, K) = G_v + (A - B) K^2 + BJ(J+1) - D_J J^2 (J+1)^2 - D_{JK} J(J+1) K^2 - D_K K^2, \quad (1)$$

where $A$ and $B$ are the rotational constants and $D_J$, $D_{JK}$, $D_K$ the centrifugal distortion constants. $G_v$ represents the vibrational energy. The $\nu_2$ band of $CH_3NC$, which is studied in this paper, is due to the $N$-$C$ stretching vibration, forming a parallel band spectrum with P-, Q- and R-branch of $\Delta K = 0$.

In the work of Thomas et al. [4] the spectra have been recorded with a grating spectrometer at a resolution of 0.15 $cm^{-1}$, just barely sufficient to recognize the rotational structure. However the main problem

Table 3. The observed and calculated wave numbers of the $\nu_2$ band of $CH_3NC$ in $cm^{-1}$.

| J | K – | J | K | OBS | CALC | O–C | SIGMA |
|---|---|---|---|---|---|---|---|
| 1 | 0 – | 2 | 0 | 2164.57482 | 2164.57585 | –0.00103 | 2.0000 |
| 1 | 1 – | 2 | 1 | 2164.57482 | 2164.57545 | –0.00063 | 2.0000 |
| 2 | 0 – | 3 | 0 | 2163.89649 | 2163.89754 | –0.00105 | 2.0000 |
| 2 | 1 – | 3 | 1 | 2163.89649 | 2163.89715 | –0.00066 | 1.0000 |
| 2 | 2 – | 3 | 2 | 2163.89649 | 2163.89597 | 0.00052 | 2.0000 |
| 3 | 0 – | 4 | 0 | 2163.21412 | 2163.21540 | –0.00128 | 3.0000 |
| 3 | 1 – | 4 | 1 | 2163.21412 | 2163.21502 | –0.00090 | 2.0000 |
| 3 | 2 – | 4 | 2 | 2163.21412 | 2163.21389 | 0.00023 | 1.0000 |
| 3 | 3 – | 4 | 3 | 2163.21412 | 2163.21199 | 0.00213 | 3.0000 |
| 4 | 0 – | 5 | 0 | 2162.52799 | 2162.52944 | –0.00145 | 4.0000 |
| 4 | 1 – | 5 | 1 | 2162.52799 | 2162.52908 | –0.00109 | 3.0000 |
| 4 | 2 – | 5 | 2 | 2162.52799 | 2162.52799 | 0.00000 | 1.0000 |
| 4 | 3 – | 5 | 3 | 2162.52799 | 2162.52617 | 0.00182 | 3.0000 |
| 5 | 0 – | 6 | 0 | 2161.83810 | 2161.83967 | –0.00157 | 4.0000 |
| 5 | 1 – | 6 | 1 | 2161.83810 | 2161.83932 | –0.00122 | 2.0000 |
| 5 | 2 – | 6 | 2 | 2161.83810 | 2161.83828 | –0.00018 | 1.0000 |
| 5 | 3 – | 6 | 3 | 2161.83810 | 2161.83652 | 0.00158 | 2.0000 |
| 6 | 0 – | 7 | 0 | 2161.14446 | 2161.14609 | –0.00163 | 4.0000 |
| 6 | 1 – | 7 | 1 | 2161.14446 | 2161.14575 | –0.00129 | 2.0000 |
| 6 | 2 – | 7 | 2 | 2161.14446 | 2161.14475 | –0.00029 | 1.0000 |
| 6 | 3 – | 7 | 3 | 2161.14446 | 2161.14307 | 0.00139 | 2.0000 |
| 7 | 0 – | 8 | 0 | 2160.44706 | 2160.44870 | –0.00164 | 4.0000 |
| 7 | 1 – | 8 | 1 | 2160.44706 | 2160.44838 | –0.00132 | 3.0000 |
| 7 | 2 – | 8 | 2 | 2160.44706 | 2160.44742 | –0.00036 | 1.0000 |
| 7 | 3 – | 8 | 3 | 2160.44706 | 2160.44581 | 0.00125 | 2.0000 |
| 8 | 0 – | 9 | 0 | 2159.74590 | 2159.74751 | –0.00161 | 4.0000 |
| 8 | 1 – | 9 | 1 | 2159.74590 | 2159.74721 | –0.00131 | 3.0000 |
| 8 | 2 – | 9 | 2 | 2159.74590 | 2159.74629 | –0.00039 | 1.0000 |
| 8 | 3 – | 9 | 3 | 2159.74590 | 2159.74475 | 0.00115 | 2.0000 |
| 11 | 0 – | 12 | 0 | 2157.61988 | 2157.62121 | –0.00133 | 4.0000 |
| 11 | 1 – | 12 | 1 | 2157.61988 | 2157.62095 | –0.00107 | 3.0000 |
| 11 | 2 – | 12 | 2 | 2157.61988 | 2157.62015 | –0.00027 | 1.5000 |
| 11 | 3 – | 12 | 3 | 2157.61988 | 2157.61882 | 0.00106 | 1.5000 |
| 12 | 0 – | 13 | 0 | 2156.90320 | 2156.90488 | –0.00168 | 4.0000 |
| 12 | 1 – | 13 | 1 | 2156.90320 | 2156.90463 | –0.00143 | 3.0000 |
| 12 | 2 – | 13 | 2 | 2156.90320 | 2156.90388 | –0.00068 | 2.0000 |
| 12 | 3 – | 13 | 3 | 2156.90320 | 2156.90262 | 0.00058 | 1.0000 |
| 13 | 0 – | 14 | 0 | 2156.18400 | 2156.18478 | –0.00078 | 2.0000 |
| 13 | 1 – | 14 | 1 | 2156.18400 | 2156.18455 | –0.00055 | 1.0000 |
| 13 | 2 – | 14 | 2 | 2156.18400 | 2156.18383 | 0.00017 | 1.0000 |
| 13 | 3 – | 14 | 3 | 2156.18400 | 2156.18264 | 0.00136 | 2.0000 |
| 14 | 0 – | 15 | 0 | 2155.46020 | 2155.46092 | –0.00072 | 2.0000 |
| 14 | 1 – | 15 | 1 | 2155.46020 | 2155.46069 | –0.00049 | 1.0000 |
| 14 | 2 – | 15 | 2 | 2155.46020 | 2155.46002 | 0.00018 | 1.0000 |
| 14 | 3 – | 15 | 3 | 2155.46020 | 2155.45890 | 0.00130 | 2.0000 |
| 15 | 0 – | 16 | 0 | 2154.73290 | 2154.73330 | –0.00040 | 1.0000 |
| 15 | 1 – | 16 | 1 | 2154.73290 | 2154.73309 | –0.00019 | 1.0000 |
| 15 | 2 – | 16 | 2 | 2154.73290 | 2154.73246 | 0.00044 | 1.0000 |
| 15 | 3 – | 16 | 3 | 2154.73290 | 2154.73139 | 0.00151 | 3.0000 |
| 16 | 0 – | 17 | 0 | 2154.00140 | 2154.00193 | –0.00053 | 1.0000 |
| 16 | 1 – | 17 | 1 | 2154.00140 | 2154.00173 | –0.00033 | 1.0000 |
| 16 | 2 – | 17 | 2 | 2154.00140 | 2154.00114 | 0.00026 | 1.0000 |
| 16 | 3 – | 17 | 3 | 2154.00140 | 2154.00014 | 0.00126 | 2.0000 |
| 17 | 0 – | 18 | 0 | 2153.26620 | 2153.26681 | –0.00061 | 1.0000 |
| 17 | 1 – | 18 | 1 | 2153.26620 | 2153.26663 | –0.00043 | 1.0000 |
| 17 | 2 – | 18 | 2 | 2153.26620 | 2153.26607 | 0.00013 | 1.0000 |
| 17 | 3 – | 18 | 3 | 2153.26620 | 2153.26514 | 0.00106 | 2.0000 |
| 22 | 0 – | 23 | 0 | 2149.53500 | 2149.53534 | –0.00034 | 1.0000 |
| 22 | 1 – | 23 | 1 | 2149.53500 | 2149.53522 | –0.00022 | 1.0000 |
| 22 | 2 – | 23 | 2 | 2149.53500 | 2149.53486 | 0.00014 | 1.0000 |
| 22 | 3 – | 23 | 3 | 2149.53500 | 2149.53424 | 0.00076 | 1.5000 |
| 22 | 4 – | 23 | 4 | 2149.53500 | 2149.53336 | 0.00164 | 3.0000 |
| 23 | 0 – | 24 | 0 | 2148.77770 | 2148.77793 | –0.00023 | 1.0000 |
| 23 | 1 – | 24 | 1 | 2148.77770 | 2148.77782 | –0.00012 | 1.0000 |
| 23 | 2 – | 24 | 2 | 2148.77770 | 2148.77749 | 0.00021 | 1.0000 |
| 23 | 3 – | 24 | 3 | 2148.77770 | 2148.77694 | 0.00076 | 1.0000 |
| 23 | 4 – | 24 | 4 | 2148.77770 | 2148.77614 | 0.00156 | 3.0000 |
| 24 | 0 – | 25 | 0 | 2148.01630 | 2148.01682 | –0.00052 | 1.0000 |
| 24 | 1 – | 25 | 1 | 2148.01630 | 2148.01673 | –0.00043 | 1.0000 |
| 24 | 2 – | 25 | 2 | 2148.01630 | 2148.01644 | –0.00014 | 1.0000 |
| 24 | 3 – | 25 | 3 | 2148.01630 | 2148.01594 | 0.00036 | 1.0000 |
| 24 | 4 – | 25 | 4 | 2148.01630 | 2148.01523 | 0.00107 | 2.0000 |

| J | K – | J | K | OBS | CALC | O–C | SIGMA |
|---|---|---|---|---|---|---|---|
| 1 | 1 – | 1 | 1 | 2165.91738 | 2165.91672 | 0.00066 | 1.0000 |
| 2 | 1 – | 2 | 1 | 2165.90793 | 2165.90905 | –0.00112 | 3.0000 |
| 2 | 2 – | 2 | 2 | 2165.90793 | 2165.90774 | 0.00019 | 1.0000 |
| 3 | 3 – | 3 | 3 | 2165.89396 | 2165.89403 | –0.00007 | 1.0000 |
| 4 | 3 – | 4 | 3 | 2165.87724 | 2165.87869 | –0.00145 | 3.0000 |
| 4 | 4 – | 4 | 4 | 2165.87724 | 2165.87559 | 0.00165 | 3.0000 |
| 5 | 4 – | 5 | 4 | 2165.85666 | 2165.85641 | 0.00025 | 1.0000 |
| 6 | 4 – | 6 | 4 | 2165.83379 | 2165.83339 | 0.00040 | 1.0000 |
| 6 | 6 – | 6 | 6 | 2165.82477 | 2165.82440 | 0.00037 | 1.0000 |
| 7 | 4 – | 7 | 4 | 2165.80714 | 2165.80654 | 0.00060 | 1.0000 |
| 7 | 6 – | 7 | 6 | 2165.79711 | 2165.79753 | –0.00042 | 1.0000 |
| 8 | 4 – | 8 | 4 | 2165.77672 | 2165.77586 | 0.00086 | 1.0000 |
| 8 | 6 – | 8 | 6 | 2165.76624 | 2165.76683 | –0.00059 | 1.0000 |
| 8 | 8 – | 8 | 8 | 2165.75406 | 2165.75392 | 0.00014 | 1.0000 |
| 9 | 4 – | 9 | 4 | 2165.74237 | 2165.74134 | 0.00103 | 2.0000 |
| 9 | 6 – | 9 | 6 | 2165.73205 | 2165.73229 | –0.00024 | 1.0000 |
| 9 | 8 – | 9 | 8 | 2165.71908 | 2165.71935 | –0.00027 | 1.0000 |
| 9 | 9 – | 9 | 9 | 2165.70957 | 2165.71134 | –0.00177 | 3.0000 |
| 10 | 1 – | 10 | 1 | 2165.70957 | 2165.70970 | –0.00013 | 2.0000 |
| 10 | 2 – | 10 | 2 | 2165.70957 | 2165.70837 | 0.00120 | 2.0000 |
| 10 | 6 – | 10 | 6 | 2165.69354 | 2165.69393 | –0.00039 | 1.0000 |
| 10 | 8 – | 10 | 8 | 2165.68080 | 2165.68095 | –0.00015 | 1.0000 |
| 10 | 9 – | 10 | 9 | 2165.67212 | 2165.67291 | –0.00079 | 1.0000 |
| 10 | 10 – | 10 | 10 | 2165.66384 | 2165.66380 | 0.00004 | 1.0000 |
| 11 | 3 – | 11 | 3 | 2165.66384 | 2165.66398 | –0.00014 | 1.0000 |
| 11 | 6 – | 11 | 6 | 2165.65132 | 2165.65173 | –0.00041 | 1.0000 |
| 11 | 8 – | 11 | 8 | 2165.63863 | 2165.63871 | –0.00008 | 1.0000 |
| 11 | 9 – | 11 | 9 | 2165.63018 | 2165.63066 | –0.00048 | 1.0000 |
| 12 | 6 – | 12 | 6 | 2165.60655 | 2165.60571 | 0.00084 | 1.0000 |
| 12 | 8 – | 12 | 8 | 2165.59258 | 2165.59265 | –0.00007 | 2.0000 |
| 12 | 9 – | 12 | 9 | 2165.58330 | 2165.58457 | –0.00127 | 2.0000 |
| 12 | 12 – | 12 | 12 | 2165.55406 | 2165.55359 | 0.00047 | 1.0000 |
| 13 | 9 – | 13 | 9 | 2165.53348 | 2165.53465 | –0.00117 | 1.0000 |
| 1 | 0 – | 0 | 0 | 2166.58901 | 2166.58781 | 0.00120 | 2.0000 |
| 2 | 0 – | 1 | 0 | 2167.25119 | 2167.25079 | 0.00040 | 1.0000 |
| 2 | 1 – | 1 | 1 | 2167.25119 | 2167.25033 | 0.00086 | 2.0000 |
| 3 | 2 – | 2 | 2 | 2167.90706 | 2167.90800 | –0.00094 | 1.0000 |
| 5 | 2 – | 4 | 2 | 2169.21470 | 2169.21461 | 0.00009 | 1.0000 |
| 6 | 2 – | 5 | 2 | 2169.86212 | 2169.86214 | –0.00002 | 1.0000 |
| 9 | 3 – | 8 | 3 | 2171.77869 | 2171.77870 | –0.00001 | 1.0000 |
| 9 | 6 – | 8 | 6 | 2171.76284 | 2171.76288 | –0.00004 | 1.0000 |
| 9 | 7 – | 8 | 7 | 2171.75511 | 2171.75510 | 0.00001 | 1.0000 |
| 9 | 8 – | 8 | 8 | 2171.74618 | 2171.74609 | 0.00009 | 1.0000 |
| 12 | 2 – | 11 | 2 | 2173.66686 | 2173.66632 | 0.00054 | 1.0000 |
| 12 | 5 – | 11 | 5 | 2173.65388 | 2173.65301 | 0.00087 | 1.0000 |
| 12 | 6 – | 11 | 6 | 2173.64664 | 2173.64597 | 0.00067 | 1.0000 |
| 12 | 7 – | 11 | 7 | 2173.63791 | 2173.63759 | 0.00032 | 1.0000 |
| 12 | 8 – | 11 | 8 | 2173.62846 | 2173.62783 | 0.00063 | 1.0000 |
| 12 | 9 – | 11 | 9 | 2173.61696 | 2173.61666 | 0.00030 | 1.0000 |
| 13 | 2 – | 12 | 2 | 2174.28537 | 2174.28683 | –0.00146 | 4.0000 |
| 13 | 3 – | 12 | 3 | 2174.28537 | 2174.28359 | 0.00178 | 4.0000 |
| 13 | 6 – | 12 | 6 | 2174.26628 | 2174.26594 | 0.00034 | 1.0000 |
| 13 | 7 – | 12 | 7 | 2174.25755 | 2174.25734 | 0.00021 | 1.0000 |
| 13 | 8 – | 12 | 8 | 2174.24737 | 2174.24733 | 0.00004 | 1.0000 |
| 13 | 9 – | 12 | 9 | 2174.23566 | 2174.23588 | –0.00022 | 1.0000 |
| 13 | 10 – | 12 | 10 | 2174.22213 | 2174.22294 | –0.00081 | 1.0000 |
| 13 | 11 – | 12 | 11 | 2174.20858 | 2174.20847 | 0.00011 | 1.0000 |
| 13 | 12 – | 12 | 12 | 2174.19329 | 2174.19241 | 0.00088 | 1.0000 |
| 14 | 2 – | 13 | 2 | 2174.90301 | 2174.90347 | –0.00046 | 1.0000 |
| 14 | 5 – | 13 | 5 | 2174.89088 | 2174.88946 | 0.00142 | 3.0000 |
| 14 | 6 – | 13 | 6 | 2174.88262 | 2174.88205 | 0.00057 | 1.0000 |
| 14 | 7 – | 13 | 7 | 2174.87369 | 2174.87323 | 0.00046 | 1.0000 |
| 14 | 8 – | 13 | 8 | 2174.86213 | 2174.86296 | –0.00083 | 1.0000 |
| 14 | 9 – | 13 | 9 | 2174.85089 | 2174.85122 | –0.00033 | 1.0000 |
| 21 | 2 – | 20 | 2 | 2179.11130 | 2179.11170 | –0.00040 | 1.0000 |
| 21 | 5 – | 20 | 5 | 2179.09586 | 2179.09513 | 0.00073 | 1.0000 |
| 21 | 6 – | 20 | 6 | 2179.08675 | 2179.08638 | 0.00037 | 1.0000 |
| 21 | 7 – | 20 | 7 | 2179.07598 | 2179.07597 | 0.00001 | 1.0000 |
| 21 | 8 – | 20 | 8 | 2179.06355 | 2179.06388 | –0.00033 | 1.0000 |
| 21 | 9 – | 20 | 9 | 2179.04947 | 2179.05006 | –0.00059 | 1.0000 |

lies in confusion caused by overlapping hot bands. We have therefore decided to use the high resolution capability of our diode laser system to remeasure the $\nu_2$ band of $CH_3NC$, with the result that in the observed region the individual $J$ lines of the fundamental band are well separated from the hot band lines. In addition, each $J$ line is accompanied by the $K$-structure, typical for symmetric top spectra. Within the Doppler limited resolution of our spectrometer, the $K$-structure has been partially resolved for the R-branch lines but not for the P-branch lines, which is understood in the very small splitting for different $K$ quantum number in this branch (< 150 MHz) and the Doppler linewidth of about 120 MHz. Typical sample spectra are shown in Fig. 3 for R- and P-branches respectively.

Where it is resolved, the $K$-structure could easily be assigned from the $K^2$ dependence of the center frequencies of lines for a given $J$ and the typical intensity pattern due to the different nuclear spin statistical

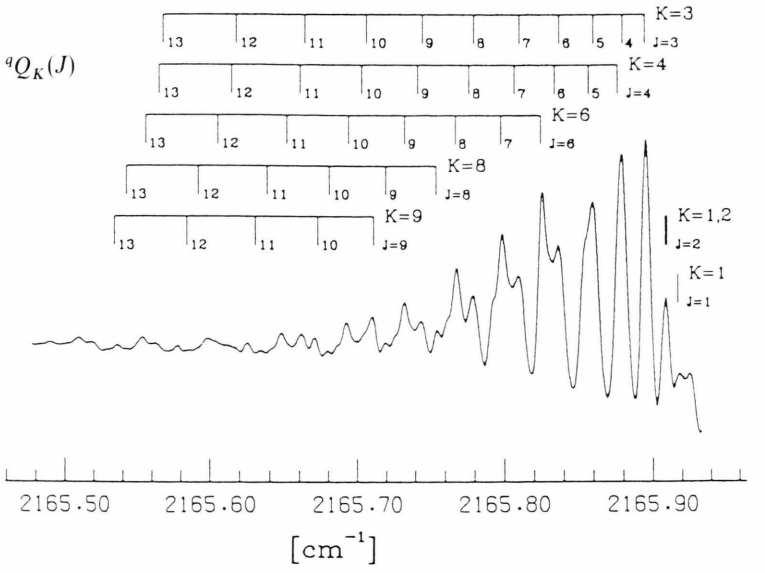


Fig. 4. The Q-branch of $CH_3NC$ $\nu_2$ fundamental band.

Table 1. The fundamental vibrations of methyl isocyanide.

| Assignment | Wavenumber [cm$^{-1}$] | Species |
|---|---|---|
| $\nu_1$ | 2965.8[a] | $A_1$ |
| $\nu_2$ | 2165.9210[b] | $A_1$ |
| $\nu_3$ | 1427[c] | $A_1$ |
| $\nu_4$ | 944.95[c] | $A_1$ |
| $\nu_5$ | 3014.3[c] | E |
| $\nu_6$ | 1463.6[c] | E |
| $\nu_7$ | 1129.7[c] | E |
| $\nu_8$ | 262.7[c] | E |

[a] Ref. (2). [b] Present work. [c] Ref. (4).

Table 2. The spectroscopic parameters of methyl isocyanide obtained for the $\nu_2$ fundamental band in cm$^{-1}$.

| Parameter | Value (Error[a]) |
|---|---|
| $\nu_0$ | 2165.92099 (13) |
| $A'-A''$ | $-0.23541\,(49)\cdot 10^{-2}$ |
| $B'$ | 0.3334103 (11) |
| $D'_J$ | $0.1474\,(19)\cdot 10^{-6}$ |
| $D'_{JK}$ | $7.626\,(14)\cdot 10^{-6}$ |
| $D'_K-D''_K$ | $0.201\,(35)\cdot 10^{-6}$ |
| $B''$ | 0.335328015 (fixed[b]) |
| $D''_J$ | $0.156107997$ (fixed[b]) $\cdot 10^{-6}$ |
| $D''_{JK}$ | $7.56189804$ (fixed[b]) $\cdot 10^{-6}$ |

[a] One standard deviation in units of the last digit.
[b] Ref. (5).

weights associated with $K=3, 6, 9, \ldots$ lines. For the first step, the resolved R-branch was identified and analysed, and then the P- and Q-branches have been assigned by a bootstrap procedure (see Figure 4). Altogether 142 transitions with proper weight have been used to fit the six parameters $\nu_0$ $(=G'_v-G''_v)$, $A'-A''$, $B'$, $D'_J$, $D'_{JK}$, $D'_K-D''_K$ with a least squares method. Here the ground state constants $B''$, $D''_J$, and $D''_{JK}$ were fixed to values obtained by a microwave study [5]. The standard deviation of the presented fit is $5.8\cdot 10^{-4}$ cm$^{-1}$. The obtained parameters are listed in Table 1, and the transitions with non zero weights for the fit are listed in Table 2.

## Discussion

The $\nu_2$ fundamental band of $CH_3NC$ shows a very compact $K$ structure. Where it is resolved, the $K$ components exhibit a regular pattern. The agreement between the observed and calculated frequencies is satisfactory for a fit over 142 partly overlapping transitions. Therefore we can conclude that there is no significant perturbation in the observed frequency range; the $N$-$C$ stretching vibration seems to be a free and undisturbed motion isolated from the other mode. It shows a strong contrast between the methyl isocyanide and methyl cyanide. The $C$-$N$ stretching mode of methyl cyanide was found to be strongly perturbed by recent diode laser studies [11, 12]. Complicated hot band structures were observed with fairly strong intensity. These lines have not yet been identified.

This work also presents an example for the application of a fast signal average technique to the TDL spectrometer for a high resolution molecular spectroscopy.

*Acknowledgements*

The averager was originally designed for the AOS spectrometer of our radio telescope at Gornergrat/Swiss by Mr. G. Schwahn. We are grateful to our electronic work shop for their help in the construction of this system and many other stuff of the telescope.

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