Sub-Doppler Saturation Spectroscopy of HCN up to 1 THz and Detection of $J = 3 \rightarrow 2$ ($4 \rightarrow 3$) Emission from TMC1

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Very high-resolution ($\sim$ 30 kHz) and very precise ($\pm$2 kHz) saturation dip and crossover dip measurements are reported for HCN. Nine consecutive rotational transitions of the vibrational ground state were recorded, covering the rotational spectrum up to the $J = 11 \leftarrow 10$ transition at 975 GHz. Commencing the saturation dip measurements with the $J = 3 \leftarrow 2$ transition located at 265 886.4 MHz, all rotational transitions were measured up to $J = 11 \leftarrow 10$ ($\Delta F = 1$), positioned at a center frequency of 974 487.2 MHz. It has become possible to resolve the hyperfine structure of every rotational transition to varying degrees. Transitions obeying the selection rules $\Delta J = 1$, $\Delta F = 0$ are have been resolved, those obeying the selection rules $J = 1$, $F = 1$ are only resolved for transitions lower than the $J = 6 \leftarrow 5$ transition.

These new experimental saturation dip data, together with the molecular beam maser emission data of the $J = 1 \rightarrow 0$ and $J = 2 \rightarrow 1$ transitions reported by De Lucia and Gordy, (Phys. Rev. **187**, 58 (1969)), and the recent terahertz measurements performed in this laboratory up to J = 22-21 at 1.946 THz (Maiwald et al., J. Mol. Spectrosc. **202**, 166 (2000)), were subjected to a least squares analysis which yielded a highly precise set of molecular constants for the ground state of HCN: B = 44 315.974 970 (156) MHz, D = 0.087 216 35 (169) MHz, H = 0.086 96 (242) Hz; eQq = –4.709 03 (162) MHz, eQq_J = 0.244 (88) Hz, C_N = 10.09 (38) kHz, C_{NJ} = –0.0143 (86) mHz.

Two constants, the hydrogen *spin*-rotation, C_H = –4.35 (5) kHz, and the *spin-spin* interaction between the proton and nitrogen nucleus, S_{NH} = 0.154 (3) kHz, can not be determined from the saturation dip measurements and have been taken from Ebenstein and Muenter, J. Chem. Phys. **80**, 3989 (1984). There also a value for the ground state permanent electric dipole moment (in Debye's) is given, which we quote for completeness: $\langle\mu\rangle_{000}$ = 2.985 188 (3) D.

We also report the discovery of the $J = 3 \rightarrow 2$ and $J = 4 \rightarrow 3$ ground state rotational transitions of HCN in the dark, cold molecular cloud TMC1 by using the KOSMA 3m-Submillimeter Telescope located in the central Swiss Alps. For the $J = 3 \rightarrow 2$ transition the hyperfine splitting has partly been resolved. The intensities of the hyperfine components are anomalous, and they are not in thermodynamic equilibrium.

Key words: Sub-Doppler Measurement; Saturation Spectroscopy; Rotational Spectrum; Submillimeter Transitions; Interstellar Molecular Spectroscopy; Dark Clouds.