A Highly Resolved Rotational Transition of Urea Measured for Radioastronomical Searches. Analysis of the Nitrogen Quadrupole Coupling

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We reinvestigated the ^{14}N quadrupole hyperfine structure (hfs) of the $J_{K_- K_+} = 1_{10} - 1_{01}$, transition of urea by use of microwave Fourier transform spectroscopy.

We resolved eight components of the hfs pattern to provide a precise laboratory experiment for possible radioastronomical searches.

The microwave ground state spectrum of urea, $CO(NH_2)_2$, was first measured and assigned by Brown, Godfrey, and Storey [1]. The rotational and centrifugal distortion constants, the μ_b dipole moment and the nitrogen quadrupole coupling constants, determined by line shape analyses, are reported in [1]. The rotational constants obtained indicate a moderately asymmetric oblate top. No transitions due to μ_a or μ_c dipole components were observed.

It is of great prebiological interest to state the existence of urea in interstellar dust clouds. The question is not yet answered. We reinvestigated the $J_{K_- K_+} = 1_{10} - 1_{01}$ transition by microwave Fourier transform spectroscopy to resolve the nitrogen quadrupole hfs, to provide precise frequencies for the hfs components to facilitate radioastronomical searches.

Our measurement gives in addition the possibility to check the former hfs analysis [1].

The sample was purchased from Merck-Schuchardt, Darmstadt, with 99.5% purity and used after vacuum sublimation at a temperature of 94 °C and a pressure of 0.13 Pa (1 mTorr).

The spectrum was recorded in the range 5.814 to 5.819 GHz at room temperature and pressures down to 0.03 Pa (0.2 mTorr). Continuous pumping was necessary to remove the remaining impurities and decomposition products.

We used a microwave Fourier transform spectrometer which was modified in comparison to that described in [2]. The local microwave oscillator was phase stabilised to a reference oscillator and the signal to the local oscillator. Details of this scheme will be published [3].

By a fault of the TWT amplifier, see part 17 in Fig. 1 of [2], we were forced to work with the signal source alone. This resulted in a remarkable decrease of sensitivity and of the range of polarization. Therefore it was not possible to polarize all components of the nitrogen quadrupole hfs pattern with one polarizing frequency. We were forced to record the multiplet of the $1_{10} - 1_{01}$ transition with eight different polarizing frequencies to get the positions of the hfs components.

The mean values of eight measured and by line contour analyses refined frequencies and their assignments are given in Table 1.

Figure 1 is composed of three of eight measured power spectra. Because of the different polarizing frequencies the relative intensities of the hfs components are not correct.

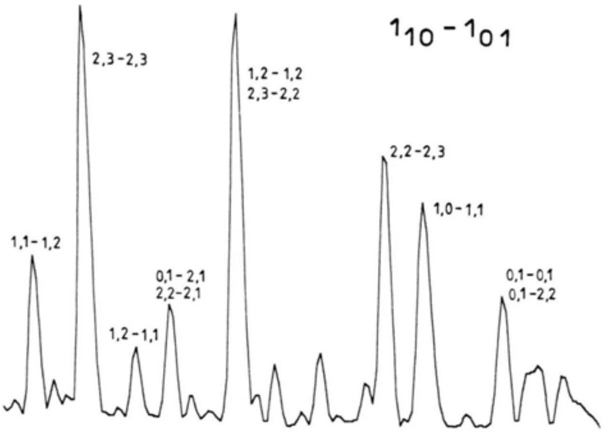

Fig. 1. $J_{K_- K_+} = 1_{10} - 1_{01}$ transition of urea, $CO(NH_2)_2$. Because of the small range of polarization three recordings with different polarizing frequencies are composed. The intensities are not correct. See text. A section of 3.6 MHz out of a 50 MHz range of the power spectra is given. Sample interval 10 ns, 64000 k cycles, 1024 data points supplemented by 3072 zeros, pressure 0.03 Pa (0.2 mTorr), room temperature.

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Table 1. Measured frequencies ν_{obs} of urea, $\mathrm{CO(NH_2)_2}$, refined by line contour analyses. The given frequencies are mean values of eight measurements with different polarizing frequencies. ν_{calc}: calculated with constants of Table 2. ν_{unsplit}: hypothetical frequency without hfs splitting. Frequencies in MHz.

$J'_{K'_- K'_+} - J_{K_- K_+} = 1_{10} - 1_{01}$

$I', F' - I, F$	ν_{obs}	ν_{calc}	ν_{unsplit}
0,1 − 2,2 0,1 − 0,1	5814.717	5814.724	5816.667
1,0 − 1,1	5815.184	5815.181	
2,2 − 2,3	5815.463	5815.465	
2,3 − 2,2 1,2 − 1,2	5816.353	5816.345	
1,2 − 1,1	5817.004	5817.006	
2,3 − 2,3	5817.296	5817.289	
1,1 − 1,2	5817.577	5817.572	
1,1 − 1,1	5818.212	5818.222	

Table 2. Quadrupole coupling constants of urea, $\mathrm{CO(NH_2)_2}$. For the hfs analysis rotational constants of [1] were taken. σ: standard deviation of the fit. $\bar{\Delta}\nu$: mean experimental splitting.

$\chi_{aa} = 2.165\ (27)$ MHz
$\chi_{bb} = 1.888\ (33)$ MHz
$\chi_{cc} = -4.053\ (50)$ MHz
$\bar{\Delta}\nu = 500$ kHz
$\sigma = 8$ kHz

correlation coefficient: $|(\chi_{aa}, \chi_{bb})| = 0.8$
$A = 11233.333$ MHz
$B = 10369.369$ MHz
$C = 5416.668$ MHz

The hyperfine structure was analysed by first order perturbation theory (programs Q2SIM and Q2FIT, modified for two equivalent quadrupole nuclei).

The coupling schema $\boldsymbol{I}_1 + \boldsymbol{I}_2 = \boldsymbol{I}$, $\boldsymbol{I} + \boldsymbol{P} = \boldsymbol{F}$ was applied. The results for the hfs analysis are given in Table 2. The standard deviation of the fit is 8 kHz for a mean experimental splitting of 500 kHz.

A comparison between the quadrupole coupling constants determined by us and by [1] shows a good agreement. One may notice that the standard errors of our coupling constants are larger than those estimated in [1]. Considering the higher resolution of our spectrum we cannot explain this point. Nevertheless we believe the frequencies measured in this work are more accurate and perhaps they will be helpful to discover urea in space.

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