The Microwave Spectrum of the Benzonitrile-Water Complex

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We report on the measurement and assignment of the benzonitrile-water complex rotational spectrum in the vibronic ground state. This study was facilitated by a newly constructed low frequency molecular beam Fourier transform microwave spectrometer.

The benzonitrile-water complex, $C_6H_5CN\text{-}H_2O$, has been investigated by laser spectroscopic methods [1, 2]. We report on the rotational spectrum in the microwave region, which provides information on the structure of the complex in the ground state and on the nitrogen nuclear quadrupole coupling.

As the complex is rather heavy, the interpretation and assignment of the spectra has been facilitated by measuring the low-J transitions between 1 and 4 GHz with a recently constructed molecular beam Fourier transform microwave spectrometer of a new design, described in [3]. The transitions in the 8 to 14.5 GHz spectral range have been accessed using the MB-FTMW spectrometer [4]. To obtain a molecular beam, a mixture of approximately 0.5% water in helium was flowed over a sample of benzonitrile upstream the beam nozzle at a backing pressure of 100 kPa. To achieve a good signal to noise ratio, averaging between 1024 and 12000 experiment cycles was mostly necessary, depending on the transition under study. 69 hyperfine components have been measured and, as an example, the $J_{K_-K_+} = 1_{01} - 0_{00}$ transition is displayed in Figure 1.

The analysis of the spectra with the model of a centrifugally distorted rotor, supplemented by nuclear quadrupole coupling [5] yields the parameters listed in Table 1. From the value of the inertia defect, $\Delta = -0.407$ amu Å^2, we conclude that the structure of the complex is almost planar if one considers the heavy atoms. Moreover, the value of the

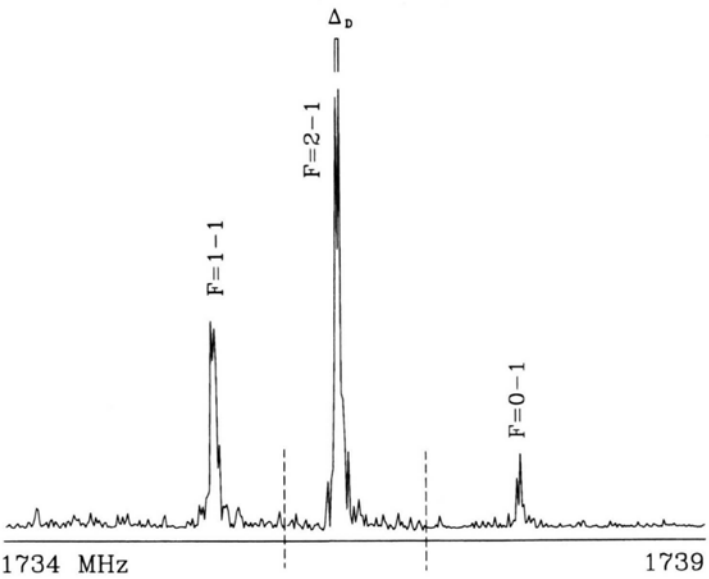

Fig. 1. The $J_{K_-K_+} = 1_{01} - 0_{00}$ transition of the benzonitrile-water complex. The quantum number F denotes the nuclear quadrupole hyperfine component. The picture consists of three recordings, separated by the dashed lines, polarized at 1735.50, 1736.37 and 1737.67 MHz. The Doppler splitting is $\Delta_D = 24$ kHz. Each measurement was taken with 6144 averaging cycles. Polarisation conditions: excitation power 1.2 mW, microwave pulse length 1.2 µs.

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Table 1. Rotational, van Eijck centrifugal distortion [7] and ^{14}N quadrupole coupling constants of the bnezonitrile-water complex. Standard errors are given in parentheses, in units of the last digit. σ standard deviation, N number of hyperfine components and $\Delta = I_c - I_a - I_b$ the inertia defect.

A	=	2882.2886 (22) MHz	R_6'	=	−0.0097 (11) kHz
B	=	995.71865 (39) MHz	χ_{aa}	=	−2.9196 (29) MHz
C	=	740.49971 (23) MHz	χ_{bb}	=	1.0824 (53) MHz
D_J'	=	0.2576 (15) kHz	χ_{cc}	=	1.8372 (52) MHz
D_{JK}'	=	−0.678 (16) kHz	σ	=	3.2 kHz
D_K'	=	4.21 (45) kHz	N	=	69
δ_J'	=	0.0874 (16) kHz	Δ	=	−0.407 amu Å^2

quadrupole coupling constant $\chi_{cc} = 1.8371\,(53)$ MHz, close to that of the benzonitrile monomer, $\chi_{cc} = 1.9498\,(32)$ MHz, [6], confirms this statement of near planarity. The measurement of C_6H_5CN-$H_2{}^{18}O$-isotopomer spectra is in progress. A more detailed discussion on the structural parameters of the complex will be presented after completing the analysis of isotopomer spectra.

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