Rotational Spectrum and ^{14}N-Quadrupole Coupling Constants of Orthofluorobenzonitrile, a Microwave Fouriertransform Study

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Seventyseven a-type rotational transitions of Orthofluorobenzonitrile were observed and assigned in the 8–25 GHz frequency range. The spectrum was recorded using the high resolution microwave Fourier transform spectrometer constructed at Kiel University. For most transitions the ^{14}N quadrupole hfs patterns could be fully resolved. The spectroscopic constants obtained by a fit to the observed hfs-center frequencies and to the observed hfs multiplet splittings are: $A = 2940.745(12)$ MHz, $B = 1512.699(1)$ MHz, $C = 998.633(1)$ MHz (rotational constants) and $\chi_{aa} = -4.114(17)$ MHz, $\chi_{bb} - \chi_{cc} = 0.383(34)$ MHz (^{14}N quadrupole coupling constants). The rotational spectrum of a low lying vibrational state could be also assigned.

Experimental

The high sensitivity, high resolution microwave Fourier transform spectrometer developed by H. Dreizler and coworkers [1, 2, 3, 4] was used to record the spectrum. The sample, a colourless liquid at room temperature, was obtained from Aldrich Chemie, Steinheim (purity > 98%) and was used after several bulb to bulb destillations to remove inert gases. Typical sample pressures within the X- through K-band waveguides absorption cells were below 2 mTorr and the cell temperatures ranged between − 20 °C and − 39 °C.

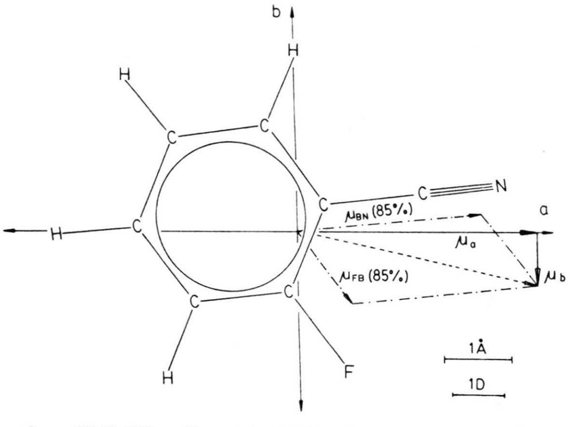
Assignment and Analysis of the Spectrum

To facilitate the assignment, the spectrum was predicted from a blend of the structures of Fluorobenzene [5], Benzonitrile [6] and 1,2-Difluorobenzene [7] as shown in Figure 1. Also shown in Fig. 1 is our first guess for the molecular electric dipole moment. It results from a vector addition of the dipole moments of Fluorobenzene [8] and Benzonitrile [9], both reduced by 15% to account for the mutual interaction of the electronegative substituents [10].

From the predicted dipole moment components, $\mu_a = 4.4$ D, and $\mu_b = 0.7$ D ($1\ \text{D} \mathrel{\hat=} 3.33564 \times 10^{-30}$ Cm), it was concluded that the a-type amplitude spectrum should be about 40 times more intense than the b-type transitions.

In Fig. 2 we present a recording of the 10868.8 MHz to 10872.8 MHz region of the spectrum in order to demonstrate the typical resolution and signal to noise ratio obtained in the present investigation.

For the vibronic ground state in total 77 different rotational transitions, most split by the ^{14}N quadru-



$A_{\text{pred.}}$: 2919.157 $B_{\text{pred.}}$: 1510.399 $C_{\text{pred.}}$: 995.379 [MHz]

Fig. 1. To scale drawing of the approximate structure, a blend of the structures of Fluorobenzene (FB) [5], Benzonitrile (BN) [6] and 1,2-Difluorobenzene [7], which was used for a first prediction of the rotational spectrum. Also given are the rigid rotor rotational constants calculated from the structure and the known atomic masses and the predicted molecular electric dipole moments (compare text).

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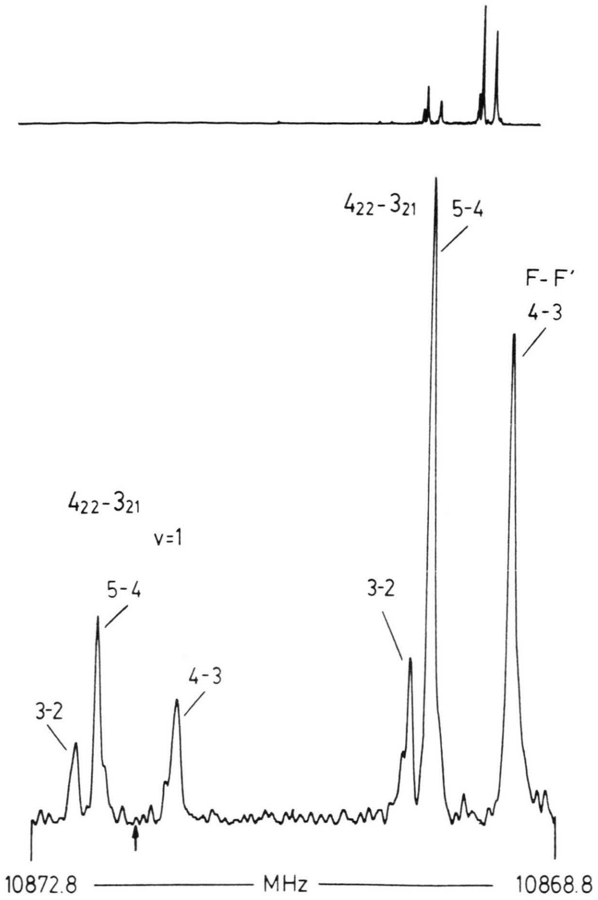

Fig. 2. 25 MHz range (top) and enlarged 4 MHz portion of the same Fourier transform power spectrum showing the $4_{22}-3_{21}$ hfs multiplets of the vibronic ground state and a low lying vibrational satellite. Note that the position of the pump frequency (indicated by the small vertical arrow) favours the polarization of the $v = 1$ satellite multiplet. – Experimental conditions were: $p = 0.4$ mTorr, $T = -23.5$ °C, pulse length: 50 ns, carrier frequency of pulse: 10 872 MHz, sampling interval: 20 ns, sampling: 1024 data points, 3072 zeros added prior to Fourier transformation, 3840 k averaging cycles.

Table 1. Some of the recorded vibronic ground state rotational transitions. The complete list is given in [17] and is available upon request. The frequencies are given in MHZ. ν_{center} are the hypothetical center frequencies of the corresponding complete hfs pattern [18]. (Note that only the strongest satellites are included in the table.) $\Delta\nu_{\text{exp}}$ are the measured splittings between adjacent satellites to which the quadrupole coupling constants (Table 2) were fitted. $\Delta\nu_{\text{calc}}$ are the corresponding splittings as calculated from the optimized molecular parameters given in Table 2. A mean square deviation of 11 kHz was obtained for the complete set of the center frequencies as well as for the complete set of the hyperfine splittings.

$J_{K_- K_+} - J'_{K'_- K'_+}$	$F-F'$	ν_{exp}	$\Delta\nu_{\text{exp}}$	$\Delta\nu_{\text{calc}}$	ν_{center}
$3_{12} - 2_{11}$	4−3	8 222.792		0.028	8 222.706
	2−1		0.335	0.316	
	3−2	8 222.457			
$4_{22} - 3_{21}$	5−4	10 869.758	0.598	0.600	10 869.595
	4−3	10 869.160	−0.745	−0.740	
	3−2	10 869.905			
$4_{04} - 3_{03}$	5−4	9 128.147		−0.024	9 128.120
	4−3		0.133	0.125	
	3−2	9 128.003			
$4_{13} - 3_{12}$	5−4	10 786.933	0.131	0.118	10 786.878
	4−3	10 786.802	−0.062	−0.049	
	3−2	10 786.864			
$4_{14} - 3_{13}$	5−4	8 827.809	0.158	0.141	8 827.750
	4−3	8 827.651	−0.096	−0.089	
	3−2	8 827.747			
$4_{23} - 3_{22}$	5−4	9 954.464	0.548	0.545	9 954.318
	4−3	9 953.920	−0.697	−0.685	
	3−2	9 954.622			
$5_{05} - 4_{04}$	6−5	11 079.220		−0.004	11 079.208
	5−4		0.068	0.065	
	4−3	11 079.152			
$5_{24} - 4_{23}$	6−5	12 301.001		−0.026	12 300.920
	4−3		0.269	0.269	
	5−4	12 300.732			
$5_{15} - 4_{14}$	6−5	10 906.548	0.074	0.044	10 906.516
	5−4	10 906.474		−0.025	
	4−3				
$10_{0\,10} - 9_{0\,9}$		20 975.357			
$10_{1\,10} - 9_{1\,9}$		20 972.897			
$11_{0\,11} - 10_{0\,10}$		22 971.454			
$11_{1\,11} - 10_{1\,10}$		22.970.514			
$11_{2\,10} - 10_{2\,9}$		24 969.989			
$12_{0\,12} - 11_{0\,11}$		24 968.136			
$12_{1\,12} - 11_{1\,11}$		24 967.790			

pole hfs interaction, were analysed in detail. In Table 1 we give a small portion of the recorded spectrum including some low J transitions (all split by the ^{14}N quadrupole hfs interaction) as well as the high J rotational transitions shown in Figure 3. The latter show very narrow hfs-multiplets which could not be resolved with our present instrumentation. (A complete list is deposited under No. TNA2, O. Böttcher and D. H. Sutter at the Universitätsbibliothek, University of Kiel.)

The spectrum was analysed by an iterative treatment of the centrifugally distorted rotor (program ZFAP4, written by V. Typke [11]) and the hfs interaction (program HT1NQ, written by G. E. Herberich [12]) similar to the procedure described in [13]. The resultant rotational constants, centrifugal distortion constants and ^{14}N quadrupole coupling constants are given in Table 2. Also given are the effective rotational constants and quadrupole coupling constants, which fit to the vibrational

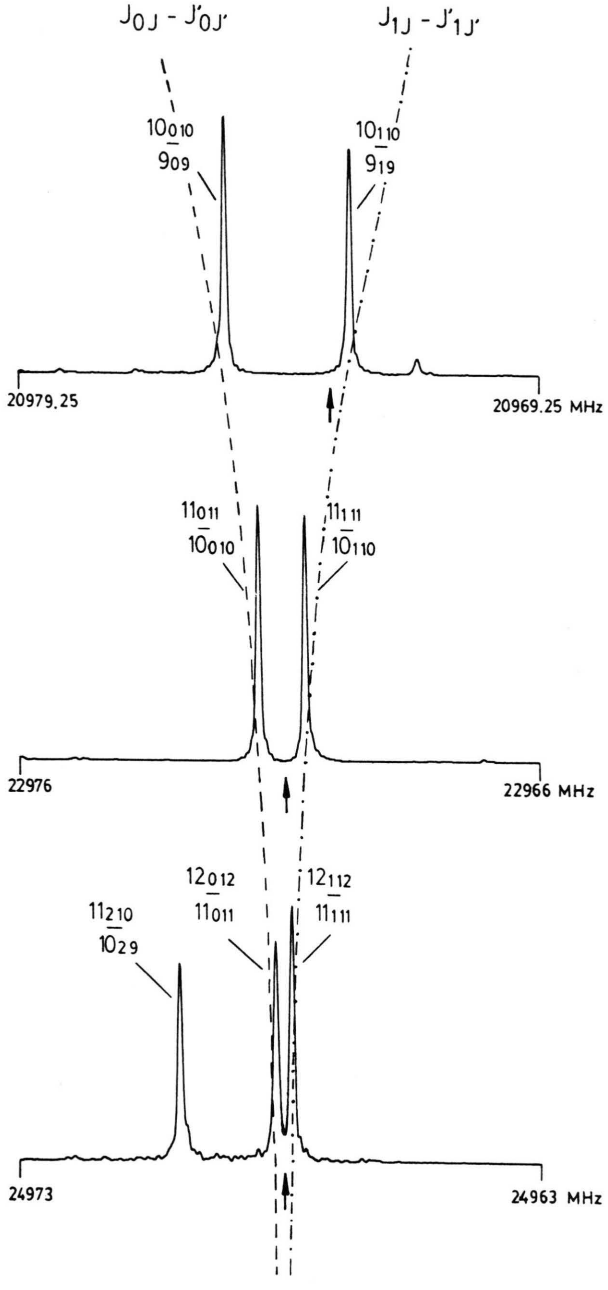

Fig. 3. Three 10 MHz sections of 50 MHz recordings in the K-band region (18–25 GHz) which show how the J_{0J}–$J'_{0J'}$ and J_{1J}–$J'_{1J'}$ rotational frequencies collapse with increasing J. (With increasing J, these maximum-K_+ transitions more and more approach the limiting oblate top case.)

Table 2. Rotational constants, centrifugal constants [11, 19] and ^{14}N-nuclear quadrupole coupling constants fitted to the complete set of 77 vibronic ground state rotational transitions observed in the present investigation (upper half), and effective rigid rotor rotational constants and quadrupole coupling constants fitted to the vibrational satellite hfs multiplets of the first excited state of a low bending vibration (most likely the V_{23} or V_{33} mode in the assignment of Green and Harrison [14]).

A	2940.745	± 0.012 MHz
B	1512.699	± 0.001 MHz
C	998.653	± 0.001 MHz
$\varkappa$	− 0.46621	
D_J	0.0261	± 0.0093 MHz
D_{JK}	0.5850	± 0.0442 MHz
D_K	− 1.0106	± 1.0400 MHz
d_1	− 0.0146	± 0.0044 kHz
d_2	− 0.0094	± 0.0024 kHz
$\chi^+ = \chi_{bb} + \chi_{cc}$	4.1141	± 0.0166 MHz
$\chi^- = \chi_{bb} - \chi_{cc}$	0.3826	± 0.0338 MHz
χ_{aa}	− 4.1141	± 0.0166 MHz
χ_{bb}	2.2484	± 0.027 MHz
χ_{cc}	1.8658	± 0.027 MHz
$A\ (v = 1)$	2941.493	± 0.830 MHz
$B\ (v = 1)$	1513.076	± 0.085 MHz
$C\ (v = 1)$	998.905	± 0.088 MHz
$\varkappa\ (v = 1)$	− 0.47063	
$\chi^+ = \chi_{bb} + \chi_{cc}$	4.239	± 0.063 MHz
$\chi^- = \chi_{bb} - \chi_{cc}$	0.437	± 0.205 MHz
χ_{aa}	− 4.239	± 0.063 MHz
χ_{bb}	2.338	± 0.152 MHz
χ_{cc}	1.901	± 0.152 MHz

Table 3. ^{14}N-hfs multiplets arising from molecules presumably in the $v = 1$ state of the lowest vibrational bending mode.

$J_{K_-K_+}-J'_{K'_-K'_+}$	$F-F'$	ν_{exp}	$\Delta\nu_{\text{exp}}$	$\Delta\nu_{\text{calc}}$	ν_{center}
$3_{12}-2_{11}$	4−3 2−1	8 225.138		0.020	8 225.044
	3−2	8 224.773	0.365	0.323	
$4_{22}-3_{21}$	5−4	10 872.326	0.615	0.620	10 872.159
	4−3	10 871.711	−0.766	−0.766	
	3−2	10 872.477			
$4_{04}-3_{03}$	5−4 4−3	9 130.362		−0.028	9 130.345
	3−2	9 130.222	0.140	0.125	
$4_{14}-3_{13}$	5−4	8 829.670	0.135	0.145	8 829.619
	4−3	8 829.535	−0.069	−0.092	
	3−2	8 829.604			
$5_{15}-4_{14}$	6−5	10 909.790	0.069	0.045	10 909.760
	5−4 4−3	10 909.721		−0.026	
$5_{24}-4_{23}$	6−5 4−3	12 303.180		−0.026	12 303.101
	5−4	12 302.914	0.266	0.277	
$5_{05}-4_{04}$		11 082.110			

satellite spectrum observed in the X-band region. From the relative intensities ($I(v=1)/I(v=0) = 0.40 \pm 0.05$) and the absolute temperature ($T = 249 \pm 2$ K for the X-band spectra), the corresponding excited vibrational state should be approximately 158(20) cm^{-1} above the ground state, which falls into the range of the 151 cm^{-1} bands assigned earlier to the V_{23} and V_{33} normal vibrations by Green and Harrison [14].

A Stark effect analysis (→ electric dipole moments), a rotational Zeeman effect analysis (→ molecular g- and susceptibility tensor and substituent effects on the field induced π-electronic ring currents [15]) and a search for at least some of the weak b-type transitions by a double resonance technique as described in [16] are planned for the near future*.

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* The "experimental frequencies" given in Table 1 are the result of lineshape analyses of the measured fouriertransform spectra. (Program SIMULINE by Merke et al., (to be published).) In these analyses arteficial transient decays with adjustable phases, initial amplitudes and decaytimes are superimposed so as to give an optimal fit of the fouriertransforms of the observed and of the arteficial transients.

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