The Microwave Spectrum of Cyanogen Iodide-^{15}N: Hyperfine Structure and Electric Dipole Moment Investigated by Microwave Fourier Transform Spectroscopy

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The first rotational transition of cyanogen iodide-^{15}N (IC^{15}N) has been investigated by microwave Fourier transform (MWFT) Stark effect spectroscopy to determine the electric dipole moment. In addition the first four rotational transitions have been measured by MWFT spectroscopy to obtain accurate parameters for the rotational, quadrupole and spin-rotation coupling parameters.

Introduction

The microwave spectrum of ICN was investigated the first time in 1947 and was the subject of a number of following papers. Townes, Holden and Merritt obtained the molecular dipole moment from an intensity measurement [1]. The first microwave data about IC^{15}N are reported in [2]. We were able to determine quadrupole- and spin-rotation coupling parameters of IC^{15}N with high accuracy using MWFT spectroscopy. The dipole moment of IC^{15}N could be obtained from MWFT Stark effect measurements using a special Stark cell and DC electric fields.

Experimental

The spectra were recorded with our MWFT spectrometers in the range from 5.0–26.5 GHz [3–6] at pressures between 0.03 and 0.13 Pa (0.25 and 1.0 mTorr) and temperatures between 243 and 253 K. For the measurements of the Stark effect a 3.25 m long cell with an 8 mm thick and 30 mm broad aluminium septum inserted was used. The cell has been manufactured from a precision J-band waveguide, 34.85 × 17.80 mm inner dimension; the construction is similar to that described in [7] for use in the X-band. The septum was milled with a precision of about 0.01 mm. The cell was calibrated by measuring the Stark effect of the $J\,K_-\,K_+ - J'\,K'_-\,K'_+ = 1\,1\,1 - 1\,1\,0$ transition of formaldehyde achieving an uncertainty of the septum position with respect to the broad waveguide walls of 0.016 mm. The dipole moment is given in [8] to be 2.33148 (2) Debye $\{7.77689\ (7) \cdot 10^{-30}$ Asm$\}$.

The sample was purchased from ALDRICH-Chemie, Steinheim.

To prepare the ^{15}N sample, 0.25 g of IC^{14}N was mixed with a few milligrams of potassium cyanide-^{15}N and a small amount was sublimated. We detected approximately 8% ^{15}N enriched substance with a mass spectrometer.

The use of the Stark cell decreased the signal strength by high cell attenuation. In addition a line broadening caused by field inhomogeneities could be noticed while applying higher DC voltages. An example is given in Figure 1.

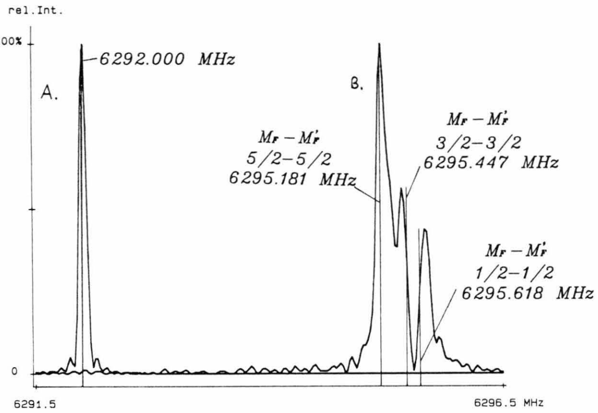

Fig. 1. Stark-effect of the $F = 5/2 - 7/2$ component of the $J = 0 - 1$ transition of IC^{15}N.
A): zero field record.
B): recorded with applied DC-field of 130.651 V/cm.
5 MHz sections out of two 50 MHz range power spectra are shown. Sample intervall: 10 ns, $0.8 \cdot 10^6$ (A) and $6.4 \cdot 10^6$ (B.) averaging cycles, 1024 data points supplemented with 3072 zeros before Fourier transformation, sample gas pressure: 1.0 mTorr (0.13 Pa), temperature: 246 K, polarizing frequency: 6291.0 MHz. In addition the frequencies obtained by fitting of the time domain signals are indicated.

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Analysis

In Table 1 the measured and calculated frequencies and the assignment of the zerofield measurements are given. Table 2 contains the measured and calculated frequencies, the assignment, DC voltages and corresponding field strengths from the Strak effect measurements.

In the case of narrow splittings the frequencies were obtained by a least squares fitting of the time domain signals [9].

The analysis of the zerofield measurements was carried out with a program based on a Hamiltonian for a linear molecule containing two unequal coupling nuclei [10]:

$$\begin{aligned}
\hat{H} &= \hat{H}_R + \hat{H}_D + \hat{H}_{Q1} + \hat{H}_{Q2} + \hat{H}_{M1} + \hat{H}_{M2}, \\
\hat{H}_R &= B\hat{J}^2, & \hat{H}_D &= -D\hat{J}^4, \\
\hat{H}_{Q1} &= -1/6\,\hat{Q}_1 : \widehat{\nabla E}_1, & \hat{H}_{Q2} &= -1/6\,\hat{Q}_2 : \widehat{\nabla E}_2, \\
\hat{H}_{M1} &= -C_{N1}\,\hat{I}_1 \cdot \hat{J}, & \hat{H}_{M2} &= C_{N2}\,\hat{I}_2 \cdot \hat{J},
\end{aligned}$$

(B rotational constant, D centrifugal distortion constant, $\hat{J}$ rotational angular momentum operator, $\hat{Q}$ nuclear quadrupole moment tensor operator, $\widehat{\nabla E}$ field gradient tensor operator, $\hat{I}$ nuclear spin angular momentum operator, C_N spin rotation coupling constant).

An angular momentum vector coupling scheme $\hat{J} + \hat{I}_1 = \hat{F}_1$, $\hat{F}_1 + \hat{I}_2 = \hat{F}$ has been used; the matrix is diagonal in the quantum number F but there are small off-diagonal elements in F_1 coming from the spin-rotation coupling of the nucleus 2. Its quadrupole coupling constant has been constrained to zero in this case. The eigenvalues were obtained by numerical diagonalization of the matrices.

The spectral parameters were obtained by a least squares fit of all values simultanously and are given in Table 3.

The analysis of the Stark effect was carried out by setting up the Hamiltonian for a linear molecule containing only one coupling nucleus:

$$\begin{aligned}
\hat{H} &= \hat{H}_R + \hat{H}_Q + \hat{H}_M + \hat{H}_S, \\
\hat{H}_R &= B\hat{J}^2, & \hat{H}_Q &= -1/6\,Q : \widehat{\nabla E}, \\
\hat{H}_M &= C_N\,\hat{I} \cdot \hat{J}, & \hat{H}_S &= -\mu E_{ST}\,\widehat{\cos(cZ)}.
\end{aligned}$$

$\widehat{\cos(cZ)}$ = direction cosine operator, μ = electric dipole moment, E_{ST} = Stark field strength.

The coupled basis representation $\hat{F} = \hat{I} + \hat{J}$ of $\hat{H}$ according to the weak-field case has been chosen. The matrix is diagonal in the quantum number M_F. The eigenvalues were obtained by numerical diagonalization of the matrices [11]. An example of an M_F-block matrix is given in Figure 2. The dipole moment of IC^{15}N was obtained by fixing all parameters in the fit derived from the more accurate zero-field measurements. The ^{15}N-spin-rotation coupling and centrifugal distortion have been neglected in this calculation. Only fully resolved M_F-splittings were used for the analysis. The results are listed also in Table 3.

Table 1. Zerofield measurements of IC^{15}N. ν: observed frequencies, δ_{o-c}: difference between observed and calculated frequencies, $\Delta\nu$: frequency shift caused by coupling of the iodine nucleus. Frequencies and frequency shifts in MHz, deviations in kHz.

J	J'	F	F'	ν	δ_{o-c}	$\Delta\nu$
0	1	2.5	2.5	5785.424	0.0	−379.933
		2.5	3.5	6292.000	−1.0	126.644
		2.5	1.5	6514.268	0.0	348.911
1	2	3.5	4.5	12384.682	0.0	53.981
		2.5	3.5	12424.555	−2.0	93.856
		1.5	0.5	12476.892	1.0	146.190
		2.5	2.5	12558.440	−1.0	227.741
		2.5	1.5	12894.241	−1.0	563.542
2	3	4.5	4.5	18081.799	0.0	−414.220
		0.5	1.5	18279.238	0.0	−216.780
		1.5	2.5	18310.790	1.0	−185.230
		2.5	3.5	18421.246	0.0	−74.772
		4.5	5.5	18525.870	0.0	29.851
		3.5	4.5	18548.500	−1.0	52.482
		3.5	3.5	18555.131	0.0	59.113
		1.5	1.5	18590.731	0.0	94.713
		2.5	2.5	18646.592	2.0	150.571
		3.5	2.5	18780.475	1.0	284.456
3	4	5.5	5.5	24250.709	−2.0	−410.587
		1.5	2.5	24568.584	0.0	−92.714
		2.5	3.5	24585.748	−1.0	−75.549
		0.5	1.5	24609.791	2.0	−51.509
		3.5	4.5	24640.467	−1.0	−20.830
		4.5	4.5	24647.097	−1.0	−14.200
		5.5	6.5	24680.238	2.0	18.939
		4.5	5.5	24694.781	0.0	33.484
		3.5	3.5	24811.090	−1.0	149.793
		4.5	3.5	24817.721	−1.0	156.424
		1.5	1.5	24826.544	1.0	165.246
		2.5	2.5	24848.526	0.0	187.228

Results and Discussion

The rotational and nuclear spin coupling parameters of IC^{15}N could be determined with high accuracy with exception of the spin rotation coupling constant of ^{15}N, because this parameter influences the spec-

Table 2. Stark-effect measurements of IC^{15}N. ν: measured frequency, δ_{o-c}: difference between observed and calculated frequencies, $\Delta\nu_{ST}$: frequency shift caused by the Stark-effect, U_{ST}: DC-voltage, E_{ST}: corresponding electric field strength. Frequencies and shifts in MHz, deviations in kHz, voltages in V and field strengthts in V/cm.

F	F'	M_F	ν	δ_{o-c}	$\Delta\nu_{ST}$	U_{ST}	E_{ST}
						0.000	0.000
2.5	2.5		5785.424	1.0	0.000		
2.5	3.5		6292.000	0.0	0.000		
2.5	1.5		6514.268	−1.0	0.000		
						10.000	26.130
2.5	2.5	1.5	5785.563	19.0	0.139		
		2.5	5785.630	17.0	0.206		
						15.000	39.195
2.5	2.5	1.5	5785.724	29.0	0.300		
		2.5	5785.881	30.0	0.457		
						20.000	52.260
2.5	2.5	1.5	5785.930	23.0	0.506		
		2.5	5786.215	31.0	0.791		
						25.000	65.325
2.5	2.5	1.5	5786.201	21.0	0.777		
		2.5	5786.646	35.0	1.222		
2.5	1.5	1.5	6514.986	15.0	0.718		
		0.5	6515.065	36.0	0.797		
						30.000	78.390
2.5	2.5	1.5	5786.527	14.0	1.103		
		2.5	5787.151	18.0	1.727		
2.5	3.5	2.5	6293.161	11.0	1.161		
		1.5	6293.261	13.0	1.261		
		0.5	6293.323	26.0	1.323		
						35.000	91.455
2.5	2.5	1.5	5786.922	16.0	1.498		
		2.5	5787.773	22.0	2.349		
2.5	3.5	2.5	6293.589	25.0	1.589		
		1.5	6293.721	22.0	1.721		
		0.5	6293.793	28.0	1.793		
2.5	1.5	1.5	6515.652	6.0	1.384		
		0.5	6515.780	19.0	1.512		
						40.000	104.521
2.5	2.5	1.5	5787.373	14.0	1.949		
		2.5	5788.486	23.0	3.062		
2.5	3.5	2.5	6294.060	17.0	2.060		
		1.5	6294.216	−2.0	2.216		
		0.5	6294.336	32.0	2.336		
2.5	1.5	1.5	6516.080	12.0	1.812		
		0.5	6516.222	3.0	1.954		
						45.000	117.586
2.5	2.5	1.5	5787.873	1.0	2.449		
		2.5	5789.263	−6.0	3.839		
2.5	3.5	2.5	6294.593	6.0	2.593		
		1.5	6294.799	−9.0	2.799		
		0.5	6294.934	18.0	2.934		
2.5	1.5	1.5	6516.555	7.0	2.287		
		0.5	6516.747	10.0	2.479		
						50.000	130.651
2.5	2.5	1.5	5788.450	4.0	3.026		
		2.5	5790.175	5.0	4.751		
2.5	3.5	2.5	6295.181	−13.0	3.181		
		1.5	6295.447	−18.0	3.447		
		0.5	6295.618	20.0	3.618		
2.5	1.5	1.5	6517.066	−16.0	2.798		
		0.5	6517.306	−11.0	3.038		
						55.000	143.716
2.5	2.5	0.5	5788.031	−10.0	2.607		
		1.5	5789.073	−7.0	3.649		
		2.5	5791.133	−32.0	5.709		
2.5	3.5	2.5	6295.847	−18.0	3.847		
		1.5	6296.161	−31.0	4.161		
		0.5	6296.361	10.0	4.361		
						60.000	156.781
2.5	3.5	2.5	6296.553	−47.0	4.553		
		1.5	6296.948	−39.0	4.948		
		0.5	6297.194	18.0	5.194		

Table 3. Rotational, nuclear spin coupling and dipole moment parameters of $IC^{15}N$. B: rotational constant, eqQ: quadrupole coupling constant, C_N: spin-rotation coupling constant, D: quartic centrifugal distortion constant, μ: electric dipole moment. Standard errors are given in units of the last digits in brackets.

A) Results of the least squares fit neglecting spin-rotation coupling of the ^{15}N nucleus.

		Correlation matrix			
B	= 3082.67965 (12) MHz	1.000			
D	= 0.540 (4) kHz	0.935	1.000		
eqQ	= −2419.9631 (28) MHz	0.185	0.230	1.000	
$C_N(I)$	= 10.08 (9) kHz	0.118	−0.085	−0.302	1.000

Standard deviation of the fit: 1.25 kHz

B) Results of the least squares fit including spin-rotation coupling of the ^{15}N nucleus.

		Correlation matrix				
B	= 3082.67943 (13) MHz	1.000				
D	= 0.540 (4) kHz	0.867	1.000			
eqQ	= −2419.9647 (25) MHz	0.271	0.263	1.000		
$C_N(I)$	= 10.02 (8) kHz	0.248	−0.026	−0.025	1.000	
$C_N(^{15}N)$	= −1.51 (49) kHz	0.568	0.199	0.215	0.271	1.000

Number of components: 30 standard deviation of the fit: 1.09 kHz

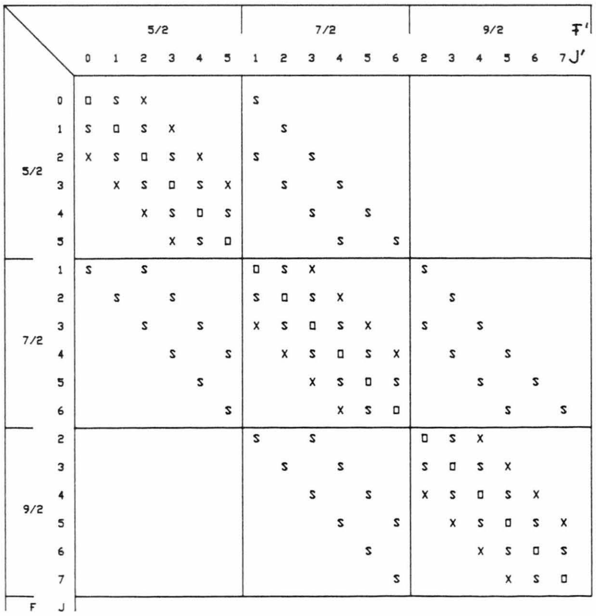
C) Results of the least squares fit of the Stark effect measurements. Only the dipole moment has been fitted, the other spectral parameters were constrained to the values of Table 3 B.

μ = 3.671 (17) D
= 12.24 (6) $\cdot 10^{-30}$ Asm

Number of components: 55; Conversion factor: $E_{ST} = U_{ST}/0.3827(16)$ cm.

Table 4. Dipole moments of cyanogen halides.

FCN [17]	2.1203 (10) D	7.0725 (33) $\cdot 10^{-30}$ Asm
^{35}ClCN [18]	2.83312 (15) D	9.45016 (50) $\cdot 10^{-30}$ Asm
^{81}BrCN [1]	2.94 D	9.81 $\cdot 10^{-30}$ Asm
$IC^{15}N$	3.671 (17) D	12.24 (6) $\cdot 10^{-30}$ Asm



	F'	5/2						7/2						9/2					
F	J \ J'	0	1	2	3	4	5	1	2	3	4	5	6	2	3	4	5	6	7
5/2	0	O	S	X				S											
	1	S	O	S	X				S										
	2	X	S	O	S	X		S		S									
	3		X	S	O	S	X		S		S								
	4			X	S	O	S			S		S							
	5				X	S	O				S		S						
7/2	1	S		S				O	S	X				S					
	2		S		S			S	O	S	X				S				
	3			S		S		X	S	O	S	X		S		S			
	4				S		S		X	S	O	S	X		S		S		
	5					S				X	S	O	S			S		S	
	6						S				X	S	O				S		S
9/2	2							S		S				O	S	X			
	3								S		S			S	O	S	X		
	4									S		S		X	S	O	S	X	
	5										S		S		X	S	O	S	X
	6											S				X	S	O	S
	7												S				X	S	O

Fig. 2. Schematic diagram of a Hamiltonian matrix for the Stark-effect of a linear molecule containing one nucleus with strong quadrupole coupling and spin $I = 5/2$. The matrix has been set up for $M_F = 5/2$ and $F = 5/2, 7/2, 9/2$ in this example. These F values are necessary for inclusion of all matrix elements containing $J = 1$. The infinite matrix is truncated at the values of $F_{max} = J + I + 1$ and $F_{min} = |J - I| - 1$ (or $F_{min} = M_F$ if $M_F \geq |J - I| - 1$).
The following parameters influence the matrix elements:
O: Rotation, quadrupole- and spin rotation coupling.
X: Quadrupole coupling.
S : Stark effect.

trum very slightly. No splittings due to ^{15}N-spin rotation coupling could be observed but the inclusion of this effect improved the fit. In Table 3 the results of this fit are compared with a second fit without inclusion of the ^{15}N spin-rotation coupling. A sign convention according to Gordy [12] has been used for the determination of the spin-rotation constants. The opposite sign is used in [13]. A small isotopic shift can be noticed comparing the iodine coupling constants of IC^{14}N and IC^{15}N [14].

The error limit of the dipole moment is constrained by the uncertainty of the septum position in the Stark cell. This uncertainty causes an error of the applied field strength. The relative errors of the field strength and the dipole moment are equal. The standard error of the dipole moment obtained from the least squares fit is about one magnitude smaller.

In Table 4 the dipole moments of some cyanogen halides are given. The values increase from FCN to ICN. The increasing dipole moments are consistent with the decreasing electronegativity of the halides assuming positive partial loads at all halogen atoms with the exception of fluorine. This is for ClCN and BrCN consistent with the direction of the dipole moment obtained by rotational Zeeman effect measurements [15, 16]. For fluorine a positive partial load at the cyano group is assumed because of the extreme electronegativity of fluorine.

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