Microwave Spectrum, Partial r_0-Structure and ^{14}N-Quadrupole Coupling Constants of 2-Cyanfurane

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The microwave spectrum of 2-Cyanfurane was investigated in the frequency range between 11 and 39 GHz. The rotational constants of the most abundant species indicate that the Cyano-group is bent toward the ring oxygen at the central C-atom. From the measured quadrupole coupling constants one may conclude that π-electron density is pulled from the ring toward the Nitrogen atom.

The rotational spectrum of 2-Cyanfurane was investigated in the frequency range between 10 and 40 GHz using a microwave spectrometer with 30 kHz Stark effect modulation described previously [1, 2]. The spectrum exhibits fairly strong a-type and weaker b-type rotational transitions with quadrupole hyperfine structure [3] due to the interaction of the ^{14}N nuclear quadrupole moment with the intramolecular electric field gradient at the position of the nucleus.

The measured frequencies listed in Table 1 were used to calculate the rigid rotor rotational constants by an iteration procedure as follows. First a set of zeroth order rotational constants $\mathbf{A}^{(0)}$, $\mathbf{B}^{(0)}$, and $\mathbf{C}^{(0)}$ was calculated from an assumed structure. For these rotational constants rigid rotor transition frequencies $\nu_{j\to j'}$ $(\mathbf{A}^{(0)}, \mathbf{B}^{(0)}, \mathbf{C}^{(0)})$ were calculated numerically together with the partial derivatives with respect to the rotational constants (compare too Ref. [4]). In this context j and j' stay for all rotational quantum numbers of the lower and upper state respectively. A first order Taylor expansion of the measured transition frequencies then led to a set of linear equations such as Eq. (1), with the corrections $\Delta\mathbf{A}$, $\Delta\mathbf{B}$, and $\Delta\mathbf{C}$ as unknowns.

$$\nu_{j\to j'\,\text{obs.}} - \nu_{j\to j'}(\mathbf{A}^{(0)},\mathbf{B}^{(0)},\mathbf{C}^{(0)}) = \left(\frac{\partial \nu_{j\to j'}}{\partial \mathbf{A}}\right)_{\mathbf{A}^{(0)},\mathbf{B}^{(0)},\mathbf{C}^{(0)}} \Delta\mathbf{A} + \left(\frac{\partial \nu_{j\to j'}}{\partial \mathbf{B}}\right)_{\mathbf{A}^{(0)},\mathbf{B}^{(0)},\mathbf{C}^{(0)}} \Delta\mathbf{B} + \left(\frac{\partial \nu_{j\to j'}}{\partial \mathbf{C}}\right)_{\mathbf{A}^{(0)},\mathbf{B}^{(0)},\mathbf{C}^{(0)}} \Delta\mathbf{C}\,. \tag{1}$$

Table 1. Rotational transitions for the most abundant species of 2-Cyanfurane in the vibrational ground state. They were used for the least squares fit of the rotational constants. Listed frequencies are intensity weighted center frequencies of the hyperfine multiplets [5].

Rotational transition $J_{K_-K_+} \to J'_{K'_-K'_+}$		ν_{obs} (MHz)	ν_{calc} (MHz)
μ_a-transitions			
2_{11}	3_{12}	11617.068	11616.932
3_{03}	4_{04}	14632.104	14632.095
3_{13}	4_{14}	14007.98	14007.965
3_{12}	4_{13}	15472.576	15472.542
4_{04}	5_{05}	18191.767	18191.803
4_{14}	5_{15}	17486.376	17486.427
4_{13}	5_{14}	19312.89	19312.865
4_{23}	5_{24}	18429.085	18429.146
4_{22}	5_{23}	18696.731	18696.815
μ_b-transitions			
3_{12}	3_{21}	21099.85	21099.500
4_{13}	4_{22}	20519.70	20519.437
4_{14}	4_{23}	23979.985	23979.726
4_{04}	5_{15}	23196.443	23196.396
4_{13}	5_{24}	38745.00	38744.883
6_{24}	6_{33}	36215.115	36215.085
7_{25}	7_{34}	35745.825	35745.988
7_{26}	7_{35}	37318.262	37318.591
7_{16}	7_{25}	18838.43	18838.682

This set of equations was subjected to a standard least squares procedure and finally led to improved rotational constants, $\mathbf{A}^{(1)} = \mathbf{A}^{(0)} + \Delta\mathbf{A}$ etc., which were used as input data for a second cycle. This procedure converged rapidly. In our case intensity averaged center frequencies of the hyperfine multiplets [5] were used as "rigid rotor frequencies" without weighting the equations for small differences in observed linewidths. The results was as follows: $\mathbf{A} = 9220.106 \pm 0.020$ MHz, $\mathbf{B} = 2029.262 \pm 0.011$ MHz, $\mathbf{C} = 1662.640 \pm 0.009$ MHz (given uncertainties are single standard deviations of the fit).

The small value of the inertia defect $I_{aa} + I_{bb} - I_{cc} = -0.103$ amu Å^2 indicates that the nuclear frame is planar. If an undistorted Furane ring [6] is assumed, a bent structure for the CN group fits best to the observed rotational constants (see Figure 1). However, this result must be regarded as only preliminary until a reliable structure can be determined from a sufficiently large set of rotational constants of different isotopic species.

The hyperfine splittings of the rotational transitions were analyzed using the first order energy

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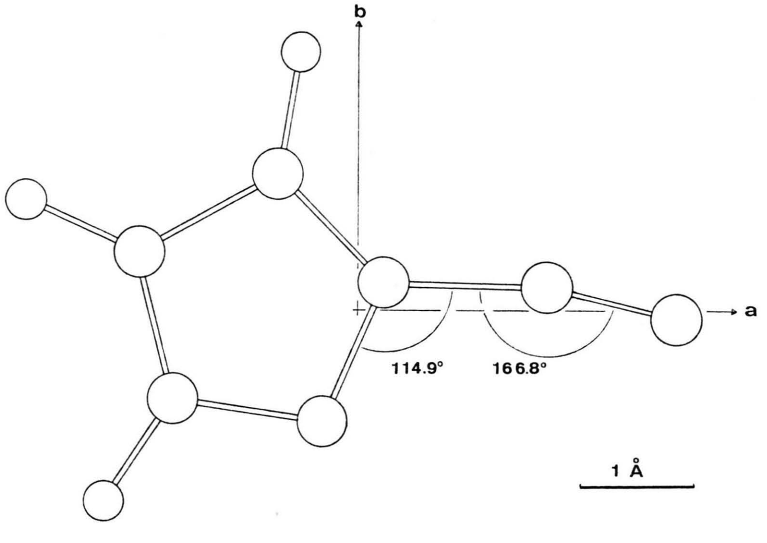

Fig. 1. Orientation of the principal inertia axes system in 2-Cyanfurane. If an undistorted Furane ring [6] is assumed together with $r_{CC} = 1.451$ Å and $r_{CN} = 1.158$ Å [11] for the CN-group, a bent C−C≡N structure with a surprisingly large bending angle of 13° fits best to the observed rotational constants. (The shown bond angles lead to $\mathbf{A}_{\text{calc.}} = 9220.104$ MHz, $\mathbf{B}_{\text{calc.}} = 2028.974$ MHz, and $\mathbf{C}_{\text{calc.}} = 1663.012$ MHz.) This result is only preliminary until a substitution structure can be determined from a sufficiently large set of rotational constants of different isotopic species.

expression for the rotational levels in the presence of one quadrupole nucleus given in Eq. (2) [7].

$$\begin{aligned} E_{J\tau IF}/h = {} & \overbrace{\mathbf{A}\,\langle J\,\tau\,\|\,\hat{J}_a^{\,2}\,\|\,J\,\tau\rangle + \mathbf{B}\,\langle J\,\tau\,\|\,\hat{J}_b^{\,2}\,\|\,J\,\tau\rangle + \mathbf{C}\,\langle J\,\tau\,\|\,\hat{J}_c^{\,2}\,\|\,J\,\tau\rangle}^{\langle J\,\tau\,\|\,\hat{\mathcal{H}}_{\text{Rot}}\,\|\,J\,\tau\rangle} \qquad (2) \\ & \underbrace{+\,\frac{\frac{3}{4}C(C+1)-J(J+1)-I(I+1)}{J(2J-1)\,I(2I-1)\,(J+1)\,(2J+3)}\left(\chi_{aa}\,\langle J\,\tau\,\|\,\hat{J}_a^{\,2}\,\|\,J\,\tau\rangle + \chi_{bb}\,\langle J\,\tau\,\|\,\hat{J}_b^{\,2}\,\|\,J\,\tau\rangle + \chi_{cc}\,\langle J\,\tau\,\|\,\hat{J}_c^{\,2}\,\|\,J\,\tau\rangle\right),}_{\langle J\,\tau\,I\,F\,|\,\hat{\mathcal{H}}_{HFS}\,|\,J\,\tau\,I\,F\rangle} \end{aligned}$$

$\mathbf{A}, \mathbf{B}, \mathbf{C}$ = rotational constants.

J, I, F = quantum numbers for the rotational angular momentum, ^{14}N-spin, and overall angular momentum respectively.

τ = quantum number used for the numeration of the $2J+1$ rotational sublevels corresponding to the same J value $(-J \leqq \tau \leqq +J)$.

$C = F(F+1) - J(J+1) - I(I+1)$.

$\langle J\,\tau\,\|\,\hat{J}_\gamma^{\,2}\,\|\,J\,\tau\rangle$ = expectation values for the squares of the angular momentum operators $\hat{J}_\gamma$ $(\gamma = a, b, c)$ in direction of the principal inertia axes, measured in units of $\hbar$, and calculated in the asymmetric rotor basis $|\,J\,\tau\rangle$ where $\hat{\mathcal{H}}_{\text{Rot}}$ is diagonal.

$\chi_{\gamma\gamma} = e\,Q\,(\partial^2 V_{\text{Coul}}/\partial\gamma^2)/h$ = quadrupole coupling constants with $e\,Q$ the nuclear quadrupole moment $(e\,Q = 4.8 \cdot 10^{-36}$ esu cm^2 for ^{14}N [8]) and $\partial^2 V_{\text{Coul}}/\partial a^2$ etc. the second derivatives of the intramolecular Coulomb potential due to the molecular charge distribution outside the nucleus $((\chi_{aa} + \chi_{bb} + \chi_{cc}) = 0$ form the Poisson Equation).

A least squares fit to the hyperfine splittings listed in Table 2 then led to:

$$(\chi_{bb} + \chi_{cc}) = 4.26 \pm 0.05 \text{ MHz and}$$
$$(\chi_{bb} - \chi_{cc}) = 0.96 \pm 0.07 \text{ MHz,}$$

Table 2. Hyperfine splittings (peak to peak frequency differences) used for the least squares fit of the quadrupole coupling constants. If unresolved hyperfine satellites are involved, as for instances in the case of the $4_{23} \to 5_{24}$ rotational transition, the fourth column gives the splitting between the well resolved satellite and the intensity weighted average frequency of the unresolved doublet.

Rotational transition $J_{K_-K_+} \to J'_{K'_-K'_+}$		Hyperfine splitting $\nu_{F\to F'} - \nu_{\tilde{F}\to\tilde{F}'}$	Observed (MHz)	Calculated (MHz)
3_{12}	3_{21}	$\nu_{3\to 3} - \nu_{4\to 4}$ $\nu_{3\to 3} - \nu_{2\to 2}$	1.229 1.631	1.199 1.619
4_{14}	4_{23}	$\nu_{4\to 4} - \nu_{5\to 5}$ $\nu_{4\to 4} - \nu_{3\to 3}$	0.500 0.606	0.505 0.608
4_{13}	4_{22}	$\nu_{4\to 4} - \nu_{5\to 5}$	0.808	0.846
4_{23}	5_{24}	$\begin{Bmatrix}\nu_{5\to 6}\\ \nu_{3\to 4}\end{Bmatrix} - \nu_{4\to 5}$	0.305	0.312
4_{22}	5_{23}	$\begin{Bmatrix}\nu_{5\to 6}\\ \nu_{3\to 4}\end{Bmatrix} - \nu_{4\to 5}$	0.333	0.294
6_{24}	6_{23}	$\nu_{6\to 6} - \begin{Bmatrix}\nu_{7\to 7}\\ \nu_{5\to 5}\end{Bmatrix}$	0.598	0.638
7_{26}	7_{35}	$\nu_{7\to 7} - \begin{Bmatrix}\nu_{8\to 8}\\ \nu_{6\to 6}\end{Bmatrix}$	0.399	0.392
7_{25}	7_{34}	$\nu_{7\to 7} - \begin{Bmatrix}\nu_{8\to 8}\\ \nu_{6\to 6}\end{Bmatrix}$	0.500	0.511

with a correlation coefficient of -0.3. Under the assumption that the symmetry axes of the quadrupole coupling tensor will closely coincide with the principal inertia axes (compare Fig. 1) i.e. assuming

$$\chi_{aa} \approx \chi_{zz}, \quad \chi_{bb} \approx \chi_{xx}, \quad \text{and} \quad \chi_{cc} \approx \chi_{yy}, \quad (\chi_{bb} - \chi_{cc})$$

may be used to give an estimate of the asymmetry of the p-electron distribution in the CN-bond. Within an approximate MO treatment[9], the above values lead to the conclusion that there is 0.064 e more electronic charge in the $2\,p_y$ atomic orbital (perpendicular to the plane) than there is in the $2\,p_x$ atomic orbital (in the plane), i.e. the CN group is pulling π-electron density from the ring. A similar difference has been found previously by Pierce et al.[10] in $S(CN)_2$ where an excess value of 0.071 e was found in the $2\,p_y$ orbital at the ^{14}N nucleus (again with the y-axis perpendicular to the molecular plane).

An analysis of the Stark effect and the rotational Zeeman effect which will give further information on the electronic structure of the molecule is under way.

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[1] H. D. Rudolph, Z. Angew. Phys. **13**, 401 [1961].

[2] U. Andresen and H. Dreizler, Z. Angew. Phys. **30**, 207 [1970].

[3] W. Gordy and R. L. Cook, Microwave Molecular Spectra, Interscience Publishers, J. Wiley, New York 1970, Chapter 9.

[4] D. H. Sutter and W. H. Flygare, The Molecular Zeeman Effect, Topics in Current Chemistry **63** [1976], Chapter II.B.

[5] H. D. Rudolph, Z. Naturforsch. **23 a**, 540 [1968].

[6] B. Bak, D. Christensen, W. B. Dixon, L. Hansen-Nygaard, J. Rastrup-Andersen, and M. Schottländer, J. Mol. Spectr. **9**, 124 [1962].

[7] see Ref. [3], Section 9.4.

[8] see Ref. [3], Appendix V.

[9] see Ref. [3], Section 14.11.c.

[10] L. Pierce, R. Nelson, and C. Thomas, J. Chem. Phys. **43**, 3423 [1965].

[11] J. Casado, L. Nygaard, and G. O. Sorensen, J. Mol. Structure **8**, 211 [1971].