

Preliminary Structure and Force Field of 4-Fluoro-benzonitrile from Microwave, Raman and Infrared Spectra

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Microwave spectra of vapours from solid 4-fluoro-benzonitrile (I), C_7H_4FN , are reported for the 18.6–39.0 GHz region and analyzed in terms of rotational and distortion constants and inertial defect $I_c - I_b - I_a$ of the ground state. Rotational constants and inertial defects for the 2 lowest vibrationally excited levels were found and analyzed. Since it is well established that the perturbing effects of one substituent such as F and CN on the benzene ring geometry is small, we present a model of I found by joining fluorobenzene and benzonitrile moieties to fit with the experimentally established rotational constants. This model would seem to represent the most rational starting structure for obtaining an *ab initio* geometry-optimized model of I. Earlier vibrational assignments are confirmed from infrared gas spectra ($3240-50\text{ cm}^{-1}$) and Raman (liq.) spectra ($50\text{ }^\circ\text{C}$) now including depolarization measurements. A quadratic force field has been constructed and used with confidence to calculate inertial defects for I and its vibrationally excited states, thus establishing an unambiguous assignment between a particular microwave spectrum and a vibrational level.

Determination of molecular structure, dynamics, dipole moment etc. are now increasingly being taken over by computers.¹ Complementary use of experimental and computer techniques is, however, still of current interest. As an example this paper wants, in the first place, to derive a 'first order' (incomplete) model of 4-fluoro-benzonitrile (I), or 1-cyano-4-fluorobenzene (Fig. 1), simply by joining moieties of fluorobenzene² and benzonitrile³ (Fig. 2). An

acceptable model should agree with the experimental rotational constants B and C of I while possessing an 'aromatic' $d \sim 1.39-1.41\text{ \AA}$. The text of Fig. 2 states this to be possible. A *para* substituted benzene such as I was chosen for its conceivable non-overlap domain C4, C6, C10 and C12 (Fig. 1), un-parallelled in *ortho* and *meta* derivatives. In the second place, a 'first-order' force field of I was obtained by the combined use of the preliminary model and of force constants for benzene, obtained *ab initio*,¹ and conventionally derived constants for fluorobenzene⁴ and benzonitrile.⁵ A complete harmonic force field for I contains 158 constants as compared to

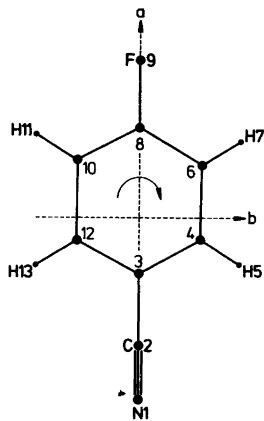


Fig. 1. Numbering of atoms in planar 4-fluoro-benzonitrile (point group C_{2v}) as applied in Fig. 2 and in Tables 6 and 7. Principal axes a, b (and c , not shown).

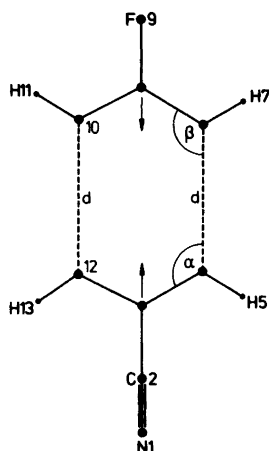


Fig. 2. Joining a fluorobenzene moiety (upper part) with a supplementary benzonitrile moiety (bottom part) to 4-fluoro-benzonitrile of C_{2v} symmetry varying the distance d . Agreement with the experimental rotational constants B and C of 4-fluoro-benzonitrile occurred for $d=1.401$ Å. $\alpha=119.3^\circ$ and $\beta=118.1^\circ$.

its 33 normal vibration frequencies, ν_i . Thus, information from other sources such as benzene are quite necessary. Adaption of the initially assumed iterative field to the normal vibration frequencies, ν_i , of I produced the desired 'first-order' field. By using this force field inertial

defects, $I_c - I_b - I_a$, for I in its ground state and in a number of vibrationally excited states could be calculated, three of them being compared to experimentally obtained defects. This linked the structural and dynamic aspects presented.

In the absence of economic restrictions a rather accurate, complete structure and force field of I could simply have been computed. The resulting molecular model would, however, not produce rotational constants (A, B, C) comparable in precision to experimental values (Table 1).

SAMPLE

Commercial I (Fluka, purity > 98 %) was used throughout, its m.p. = 32–34 °C and its IR spectrum being as published.⁶ Its equilibrium vapor pressure, νp_{eq} , is 0.65 and 0.20 Torr at 25 and 0 °C, respectively (LKB Autovac). If I was kept at liquid nitrogen temperature for 2–3 h. followed by spontaneous heating to room temperature, a higher νp was observed, slowly decreasing to 0.65 Torr at 25 °C. Possibly, more than one crystalline form of I exist.

MICROWAVE SPECTRA. ASSIGNMENTS. DIPOLE MOMENT.

Microwave (mw) spectra of I have not yet been reported. They were recorded in a 'flow' system

Table 1. Calculated (ROTFIT⁸) ground state rotational constants A, B, C , (MHz) and distortion constants (τ_{aaaa} etc.) in kHz of 4-fluoro-benzonitrile from 65 experimental $J_{K_1} K_{+1} \rightarrow J_{K_1-1} K_{+1} + 1$ ($9 \leq J \leq 22$) microwave transitions between 18.4 and 40 GHz.^a RMS deviation 0.031(3) MHz. Asymmetry parameter $\kappa = -0.94028(3)$. Inertial defect^b $I_c - I_b - I_a = 0.016(2) \mu\text{Å}^2$. Identification frequencies (MHz), ANALYT.

A	B	C		
5627.638(59)	972.39469(120)	829.10806(86)		
τ_{aaaa}	τ_{bbbb}	τ_{cccc}	τ_{abab}	τ_{caca}
-1.000(fixed)	-0.0810(90)	-0.0406(31)	-0.5272(18)	0
-4.755 ^c	-0.0896 ^c	-0.0428 ^c	-0.6543 ^c	0
ANALYT				
Transition	Experimental			Exp-Calc.
$10_{2,8} \rightarrow 11_{2,9}$	20317.38(20)			0.001
$14_{2,12} \rightarrow 15_{2,13}$	27941.74(20)			-0.005
$17_{2,15} \rightarrow 18_{2,16}$	33571.76(20)			0.130
$20_{2,19} \rightarrow 21_{2,20}$	37078.13(20)			-0.026

^a Available on request. ^b Conversion factor 505376 uÅ^2 . Inertial defect from vibrational spectra, 0.028 uÅ^2 . ^c From vibrational spectra.

described earlier,⁷ at cell temperatures 25° and pressure $p=30$ mTorr, and at *ca.* -60 °C ($p=3-5$ mTorr). The results obtained by pumping I(gas) through a conventional Stark modulated cell are reported in Table 1. 65 ground state transitions were measured of which only 4 prominent lines are included for identification purposes. The numerically small inertial defect shows I to be planar as expected. In addition, the observed intensity alternation, 5:3 for K_{-1} even: odd, agreed with spin exchange of two pairs of equivalent protons about a C_2 axis. Thus, I has at least C_{2v} symmetry.

The microwave spectra of I at 25 °C had rather intense patterns of vibrational satellites, due to low-energy vibrational states (Table 2) and to a large dipole moment. Experimental dipole moments of gaseous fluorobenzene and benzonitrile are 1.59 and 4.39 D, respectively.⁹ A predicted dipole moment of I would be 2.80 D. The conveniently located transition $10_{2,8} \rightarrow 11_{2,9}$ (Table 1) showed 5 distinct Stark lobes towards lower frequencies not coinciding with the satellite pattern concerned at higher than 20318 MHz. For $M=0,1,2,3,4$ the shifts were -2.57, -4.06, -9.14, -17.28 and -28.78 MHz fitting with a dipole moment of 2.88 ± 0.05 D (program STARK⁸). The measurements were taken at -60°, $p=3-5$ mTorr and at 2924 V cm^{-1} electric field intensity.

Based partly on an assignment of normal vibration frequencies of I (*vide infra*), Table 2

predicts relative mw spectral intensities and inertial defects of I in its ground state and in 9 moderately populated vibrationally excited levels, thus suggesting the working strategy to be applied. For each ' K_{-1} even' mw transition (Table 2, Int^c) the ground state line is easy to distinguish even at room temperature (see Table I, ANALYT) whereas the satellites are much harder to assign. To identify ' K_{-1} odd' ground state transitions, cooling of the mw cell is necessary (Table 2, Int^d). Hereafter, Table 1 resulted. The ' K_{-1} odd' transitions for molecules in the level at 104 cm^{-1} could subsequently be identified at 25° because of their high intensity. This produced rotational constants permitting calculation of ' K_{-1} even' transitions and subsequent experimental location. The experimental $I_c - I_b - I_a$ of $-1.66(3) \text{ u}\text{\AA}^2$ is in satisfactory agreement with $-1.59 \text{ u}\text{\AA}^2$ from vibrational data (Table 3). The mw spectrum of I in the level at 152 cm^{-1} was analyzed correspondingly (Table 3). The rotational constants of vibrationally excited levels are less accurate than for the ground level, partly due to Stark lobe perturbances. The analyses for further satellite spectra will be postponed.

VIBRATIONAL SPECTRA. NORMAL VIBRATION FREQUENCIES.

Raman and IR spectra of dissolved I have been published earlier and analyzed in terms of 33

Table 2. Energies (cm^{-1}) of the lowest vibrational levels of 4-fluorobenzonitrile from IR and Raman spectra, E; normal vibration numbers as in ref. 6, i; sum levels, Sums; 'Boltzmann' population at 300K, Boltz; C_{2v} vibrational species $a_1(e)$, $b_2(o)$, $a_2(e)$, $b_1(o)$, even-odd referring to C_2 ,^{a,b} Species; spin weight factors for K_{-1} even or odd, $S(e)$ and $S(o)$; relative intensities, Int; calculated inertial defects, i.d. in $\text{u}\text{\AA}^2$.

E	i	Sums	Boltz	Species ^b	$S(e)$	Int ^c	$S(o)$	Int ^d	i.d.
0			1.00	$a_1(e)$	5	1.00	3	0.60	+0.028
104	22		0.59	$b_1(o)$	3	0.35	5	0.58	-1.59
152	33		0.47	$b_2(o)$	3	0.28	5	0.47	+1.49
208		2×22	0.35	$a_1(e)$	5	0.35	3	0.21	-3.21
256		22+33	0.28	$a_2(e)$	5	0.28	3	0.17	-0.13
265	21		0.26	$b_1(o)$	3	0.16	5	0.27	-0.48
304		2×33	0.22	$a_1(e)$	5	0.22	3	0.13	+2.95
312		3×22	0.21	$b_1(o)$	3	0.13	5	0.22	-4.83
360		2×22+33	0.17	$b_2(o)$	3	0.10	5	0.17	-1.75
369		21+22	0.15	$a_1(e)$	5	0.15	3	0.09	-2.10

^a Axis of minimum moment of inertia. ^b Capital letters, A_1 , B_2 , A_2 , B_1 used in most literature. ^c ' K_{-1} even' transitions. ^d ' K_{-1} odd' transitions.

Table 3. Calculated (ROTFIT⁸) rotational constants A, B, C (MHz) for the two lowest vibrational levels at 104 and 152 cm^{-1} , respectively, of 4-fluoro-benzonitrile based on 39 and 43 experimental microwave transitions; vibrational levels in cm^{-1} , Levels; rms deviations, r.m.s.; experimental inertial defects, i.d., in $\text{u}\text{\AA}^2$.

Levels	A	B	C	r.m.s.	i.d. ^a
104	5545.0(1.1)	973.203(17)	830.153(14)	0.4575(563)	-1.66(3)
152	5705.5(1.2)	973.570(17)	829.629(14)	0.4680(544)	+1.49(3)

^a Calculated from force field -1.59 and +1.49 $\text{u}\text{\AA}^2$, respectively.

Table 4. Distribution of 4-fluoro-benzonitrile normal vibrations ν_i on C_{2v} species a_1, b_2 (planar), a_2 and b_1 , Species; Raman polarization (pol/depol), Pol; i.r. activity (\pm), i.r.; band contour branches P, Q, R ; types A, B, C, TYPE ($\kappa = -0.94$, Table 1).

Species	i^a	Pol ^b	i.r.	P, Q, R^b	TYPE
a_1	1-12	pol	+	PQR	A
b_2	23-33	depol	+	PR	B
a_2	13-15	depol	-		
b_1	16-22	depol	+	P^cQR^c	C

^a Numbered as in ref. 6. ^b Experimental spectra, available on request. ^c Weak. Q -branch dominates.

normal vibration frequencies, ν_i ($i=1-33$), distributed on C_{2v} species a_1, b_2, a_2 and b_1 .⁶ To ensure that no serious disagreement concerning the ν_i 's of Ref. 6 exists, readily available Raman equipment was used by us to obtain Raman spectra (50-3200 cm^{-1}) of I (liq.) at 50 °C, and IR spectra at 25 °C of I(gas) at $p=0.60$ Torr, recorded interferometrically 50-500 cm^{-1} (path length 4.6 m) and conventionally 400-3240 cm^{-1} (path length 20 m). The expected spectral features are reported in Table 4, the assignments of ν_i 's in Table 5. Referring to Ref. 6, Table 2, page 1282, acceptable agreement was obtained comprising our measurements of Raman line polarization and i.r. band contours (not explicitly reported in Ref. 6). Only a few questions remain. We suggest to replace $\nu_{22}=118 \text{ cm}^{-1}$ by the FIR observed 104 cm^{-1} (Fig. 3) for I(gas). Further, we definitely interpret the contour of the IR spectrum around 540 cm^{-1} as necessarily due to a C -type band (b_1 species) superimposed by a B -type band (b_2) excluding the presence of A -type contour. Thus, $\nu_{31}=540 \text{ cm}^{-1}$. The three IR inactive a_2 vibrations ν_{13}, ν_{14} and ν_{15} are Raman active. Within the limits of the reliability of our force field (*vide infra*) their predicted locations are at 965, 840 and 392 cm^{-1} . Observed

polarized Raman bands at 948 (weak), 840 (strong) and 400 cm^{-1} (strong) might hide weak depolarized ν_{13}, ν_{14} and ν_{15} .

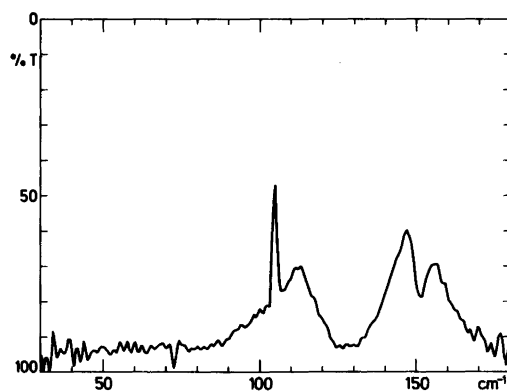


Fig. 3. Far infrared spectrum of gaseous 4-fluorobenzonitrile obtained interferometrically by subtraction of an experimental 'background' of 4 superimposed runs from 3 averaged interferograms of I(gas). No further bands were observed 160-400 cm^{-1} . $\nu_{21}=269 \text{ cm}^{-1}$ was seen only in Raman (Table 5).

Table 5. Present assignment of 4-fluor-benzonitrile gas phase normal vibration frequencies (cm^{-1}) ν_i numbered as in ref. 6. If unobserved in the IR gas spectrum the uncorrected value from the Raman spectrum (liq.) has been inserted marked by Ra. C_{2v} species a_1 , b_2 , a_2 , b_1 .

a_1 -species			b_2 -species			a_2 -species			b_1 -species		
Exp.	i	Calc. ^c	Exp.	i	Calc. ^c	Exp. ^a	i	Calc. ^c	Exp.	i	Calc. ^c
3081	1	3085	3078	23	3081	—	13	965	922	16	948
3062	2	3061	3062	24	3064	—	14	840	842	17	822
2240	3	2242	1607	25	1616	—	15	392	728	18	740
1612	4	1620	1407	26	1419	—			538	19	537
1514	5	1510	1300	27	1312	—			Ra 469	20	472
1253	6	1262	1245	28	1260	—			Ra 269	21	265
Ra 1193	7	1210	1095	29	1118	—			104	22 ^b	106
1159	8	1147	Ra 645	30	638	—					
1018	9	1019	540	31	540	—					
838	10	830	405	32	404	—					
678	11	688	152 ^b	33	152	—					
411	12	398									

^a See text. ^b Calculated inertial defect in Table 3. ^c From Table 6 ADAPT constants.

Table 6. Adopted (ADOPT) and adjusted (ADAPT) force field constants for 4-fluoro-benzonitrile (Fig. 1). Experimental and calculated normal vibration frequencies in Table 5. Possible alternative, ALTER.

Deformations	Units	ADOPT	ADAPT	ALTER
Stretchings	mdyn/Å			
C-F		5.80 ⁴	5.77(52)	7.1(9)
C-N		16.80 ⁵	16.1 ^a	17.0(8)
C2-C3		5.39 ⁵	7.18(57)	5.39(fixed)
Angles (in plane)	mdyn Å			
β -CF ^b		1.89 ⁴	1.99(7)	
β -C3C2 ^b		1.36 ⁵	1.09(8)	
\angle CCN		0.35 ⁵	0.42(3)	
Interactions (in plane)				
C-F/C6-C8	mdyn/Å	0.43 ⁴	0.54(25)	
C2-C3/C3-C4	—	0.18 ⁵	0.2 ^a	
C-F/ q_{19}^c	mdyn	-0.11 ¹	-0.39(21)	
C-F/ q_{20a}^c	—	-0.10 ¹	-0.66(28)	
β -CF/ β -CH ^b	mdyn Å	0.02 ¹	0.13(5)	
β -C3C2/ β -CH ^b	—	0.02 ¹	-0.21(6)	
Angles (out of plane)				
γ -CF	mdyn Å	0.6	0.54(7)	
γ -C3C2	—	0.48 ⁵	0.38(5)	
\angle CCN	—	0.37 ⁵	0.49(7)	
γ -C3C2/ \angle CCN	—	0.01 ⁵	-0.05(3)	

^a Fixed, but changed in succeeding calculations until optimal fit was obtained. ^b β is defined as in Ref. 4; for example, β -CF is defined as $\frac{1}{2}(\angle C6C8F - \angle C10C8F)$. For sign conventions see Ref. 1 and 4. ^c See ref. 1.

Table 7. Preliminary structure of 4-fluoro-benzonitrile (rotational constants B_{mod} and C_{mod} MHz) agreeing with experimental B and C (Table 1). Selected structure elements from fluorobenzene² and benzonitrile.³ Atom numbering in Fig. 1, fragments approach in Fig. 2.

Distances	(Å)	Angles (degrees)	
N≡C	1.1581 ^a	C3C4H5	120.64 ^a
C2C3	1.4509 ^a	C4C3C12	121.82 ^a
C3C4	1.3876 ^a	C3C4C6	119.30 ^c (α)
C4H5	1.0803 ^a		
C4C6	1.401 ^c (d)	C6C8C10	123.4 ^b
FC	1.354 ^b	C8C6H7	120.0 ^b
C6C8	1.383 ^b	C8C6C4	118.1 ^c (β)
C6H7	1.081 ^b		
	B^d	C^d	
	972.394	829.108	
	B_{mod}	C_{mod}	
	972.120	829.429	

^a Ref. 3. ^b Ref. 2. ^c Derived parameters d, α , β . ^d Table 1.

CHOICE AND CHECK OF FORCE FIELD

A tentative force field for I (C_{2v}) was constructed by first redistributing the quantum mechanically calculated field for benzene (D_{6h})¹ according to C_{2v} symmetry, the result being checked by satisfactory recalculation of the benzene normal frequencies (VIBROT⁸). Hereafter, values of force field constants from Ref. 4 and 5 connected with the substituents F and CN, respectively, were introduced (Table 6, ADOPT), taking the remaining necessary constants from Ref. 1. For the redundant set of ring CC stretch and CCC bending coordinates, symmetry coordinates were used.^{1,4} The benzene part of the field was unchanged during a following least-square fit (FLINDA⁸) except for the constants under ADOPT, Table 6. The adapted constants are reported in Table 6, ADAPT, stating possible numerical values of the desired tentative force field constants. The corresponding v_i 's are reported in Table 5 showing acceptable agreement with the assigned v_i 's. The ADAPT constants produce satisfactory agreement between calculated and experimental inertial defect (~ 0) and the distortion constants τ_{aaaa} etc. for I in its ground level (Tables 1 and 2), and between the inertial defects of I in its v_{22} and v_{33} levels (Table 3). Thus, the remaining inertial defects given in Table 2 may prove useful for future work.

DISCUSSION

Table 7 summarizes assumed and calculated geometric parameters of I assembled as in Fig. 2. The resulting $d=1.401$ Å, $\alpha=119.3^\circ$ and $\beta=118.1^\circ$. The C3–C8 distance is 2.7309 Å compared to 2.7338 Å in $C_6H_5NO_2$.¹⁰ The ADAPT field is, of course, far from unique and only moderately different from expectations except, perhaps, the C2–C3 stretching constant of 7.18 mdyn/Å. It is larger than in benzonitrile (5.39)⁵ and in *p*-chloro-benzonitrile (6.0)¹¹ and actually quite comparable to the C–C stretching constant in benzene. Taking the C2–C3 constant at its 'face' value of 7.85 suggests taking a shorter C2–C3 distance than assumed (1.45 Å, Table 7). Simply taking it from vinylcyanide, $N\equiv C-CH=CH_2$,¹² where C–C is 1.425 Å and proceeding as above, leads to $d=1.420$ Å, $\alpha=119.3^\circ$ and $\beta=118.1^\circ$. If felt necessary, an 'aromatic' d in the 1.39–1.41 Å range is easily obtainable by small adjustments of the chosen fluorobenzene and benzonitrile fragments. As shown in column ALTER of Table 6 a similar discussion could be centered around the force constant and the assumed length of the C8–F bond, 'freezing' the C2–C3 stretching constant at the benzonitrile value (5.39). The force constants of C–F, $C\equiv N$ and C2–C3 stretchings are strongly correlated. Presently we have no intention of going further.

Acknowledgements. The Danish National Science Research Council is acknowledged for its support. Thanks are due to N. W. Larsen, T. Pedersen and G. O. Sørensen of this laboratory for helpful discussions.

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Received November 26, 1982.