The purification of **15** and **50** has been described previously.[11] Crystalline samples of **2**,[46] **3**,[47] **5**,[48] **7**,[49] **8**, **10**, and **11**,[38] **17**,[50] **18**,[51] **19**,[34] **20**,[23] **21**,[24] **25**,[21] **26**,[17] **27**,[18] **29**,[26] **30**,[52] **31**,[12] **32**,[19] **33**,[9] **36**,[53] **37**,[54] **38**,[55] **39**,[56] **40**,[57] **41**,[58] **44** and **45**,[59] **46**,[60] **48**,[61] **49**,[62] and **51**[63] were obtained by using the methods described in the papers reporting their X-ray structures or syntheses.

The syntheses of **9**,[64] **12**,[65] **13**,[66] **14**,[67] **22**,[68] **24**,[69] **28**,[10] **35**,[11b] and **47**[70] have been described. Compound **12** was recrystallized from acetone, **13** from hot methanol, and **24** from $CHCl_3$. Compound **32**[19] was prepared by the combination of benzene solutions containing equimolar amounts of Me_2SnCl_2 and salicylaldehyde. Concentration of the solution gave pale yellow crystals (mp 55 °C) of **32**. Compound **16** was prepared from Me_3SnCl and $NaS_2CNMe_2{\cdot}2H_2O$ with the method Bonati and Ugo[71] described for the synthesis of $Et_3Sn(S_2CNEt_2)$. Recrystallization from acetone–hexane solution gave needles with mp 58–61 °C (lit.[72] mp 63 °C).

The unit cells of crystalline **19** and **29** were determined to confirm their identification.

NMR Spectroscopy. Solid-state ^{13}C NMR spectra were obtained on ca. 0.4 g of polycrystalline or amorphous methyltin(IV) compounds at 15.08 MHz with 60 MHz high-power proton decoupling. Magic angle spinning at 2300 Hz in an Andrew-type rotor and spin-locking cross-polarization with the ^1H and ^{13}C fields matched at 57 kHz for 2 ms were used to obtain high-resolution solid-state spectra. With dwell times of 50 μs and repetition rates of 3–20 s, generally 3 to 20 k scans were required to determine $|^1J|$. Chemical shifts (±0.3 ppm) are referenced to the internal secondary standard, delrin [89.1 ppm (Me_4Si = 0 ppm)]. The solution ^{13}C NMR spectrum of **26** was obtained on a DMSO-d_6 solution at 100 MHz on a Bruker WM-400 spectrometer (400 MHz for ^1H). $|^1J|$ was 691.1 Hz and $|^2J|$ was 76.7 Hz at 304 K.

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Microwave Spectrum, Inversion, and Molecular Structure of Monofluoramine, FNH_2

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Abstract: Microwave spectra of a new molecule, monofluoramine, and its deuteriated isotopomers have been recorded and analyzed, yielding data on the molecular structure, dipole moment, quadrupole coupling, and barrier to inversion. The results are the following: A = 263 271.534 MHz, B = 26 357.357 MHz, C = 25 329.428 MHz, μ_a = 1.58 D, μ_c = 1.63 D, μ_{total} = 2.27 D, χ_{aa} = 7.16 MHz, χ_{bb} = −0.61 MHz, χ_{cc} = −6.55 MHz for the protonated species. The structural parameters are as follows: r_{NF} = 143.29 pm, r_{NH} = 102.25 pm, ∠FNH = 101.08°, ∠HNH = 106.27°, H_{INV} = 5200 cm^{-1}.

In recent years the investigation of substituted ammonia has aroused considerable interest due to an increased understanding of the effect of the inversion motion on the molecular spectra. As to the elucidation of the electronic properties that govern the inversion motion in a double minimum potential, one hopes that the analysis of the molecular spectra of simple amines will provide a better understanding.

Many of the simple amines, however, possess additional large amplitude motions (lam), which can considerably complicate the microwave spectra and blur the meaning of the inversion motion, as in H_2NNH_2[1] or H_2NCN.[2] There are cases, however, where these complications apparently do not arise, as in H_2NOH,[3] H_2NNO_2,[4] and H_2NNC,[5] but in order to isolate the inversion motion, only molecules with one H atom substituted by another atom should be considered. Until now, the only member of this

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group of molecules (except for deuteriated ammonia[6]) was H_2NCl.[7] We have now added H_2NF. This molecule is also the last member of the series NH_3, FNH_2, F_2NH, and F_3N to be synthesized and investigated, thus permitting a determination of the effect of successive fluorination of NH_3.

Experimental Section

FNH_2 was produced by low-temperature (−30 °C) pyrolysis of the monofluoroammonia salt $H_3NF^+HF_2^-\cdot nHF$, which is stable below its melting point (170 K).[8] The gas was introduced in a steady flow to the microwave absorption cell through an activated potassium fluoride filter[9] for selective hydrogen fluoride absorption.

After 2–3 days, the cell had been conditioned and the FNH_2 was quite stable at pressures around 6–8 mTorr, but up till then hardly any signal was detected.

There were, however, always lines due to other substances present in the cell, and the identified lines are only a fraction of the recorded ones. For the deuteriated species, a rapid proton exchange was noted, and with hindsight, the deuteriated species could have been investigated with less labor by dosing the cell with D_2O vapor and using a sample of the normal (protonated) species as precursor instead of synthesizing them directly.

After a while, ammonia and all deuteriated ammonias were always present in the cell.

Spectroscopic Analysis. The observation of the microwave and millimeter wave spectra was performed with a conventional 100 kHz Stark modulated microwave spectrometer with a 5 m X-band aluminum waveguide cell. Microwave spectra (X-, Ku-, and K-band) were measured with Marconi sweepers (6600A) phase locked to a harmonic of a Schomandl ~1 GHz quartz controlled oscillator, whereas millimeter wave spectra between 44 and 104 GHz were recorded with use of a two-stage synchronization scheme, phase locking an OKI klystron to the 2nd, 3rd, or 4th harmonic of a stabilized Marconi sweeper operating between 22 and 30 GHz. All spectra were recorded directly.

Results

Analysis of the Spectra. FNH_2 is a pyramidal, asymmetric near-prolate rotor with an AC symmetry plane and the possibility of inversion, i.e., the E* operation of the Longuet–Higgins permutation–inversion group is not a completely feasible symmetry operation.[10]

Thus, depending on the inversion barrier heights, the molecule will possess C_s symmetry (very high barrier) or belong to a symmetry group isomorphic with $C_{2v}(M)$[11] (a barrier so low as to allow for tunneling rates on the time scale of the experiment, leading to a planar reference configuration). In the latter case, vibrational states will split by an amount that depends on the heights of the barrier into symmetric v^+ and antisymmetric v^- inversion components with different spin statistics. Possible microwave transitions are intra-state (inversion invariant) μ_a transitions connecting rotational states within either symmetric or antisymmetric inversion states and inter-state (inversion variant) μ_c transitions connecting inversional states of different parity and split by twice the amount of the v^+–v^- splitting.

A comparison with the microwave investigation of H_2NCl[7] predicts the barrier to inversion to be sufficiently high to cause small v^+–v^- splittings and virtually identical rotational constants in the split states, yielding a rigid rotor μ_a spectrum and two rigid rotor μ_c spectra probably split by less than a few hundred MHz, whose relative intensities only depend on spin statistics.

The rotational constants B and C to a great extent only depend upon the length of the NF bond, which will virtually lie on the A axis. Consequently, the μ_a spectrum can be confidently predicted by using a reasonable model, based on the known structures of NH_3,[12] F_2NH,[13] and F_3N.[14]

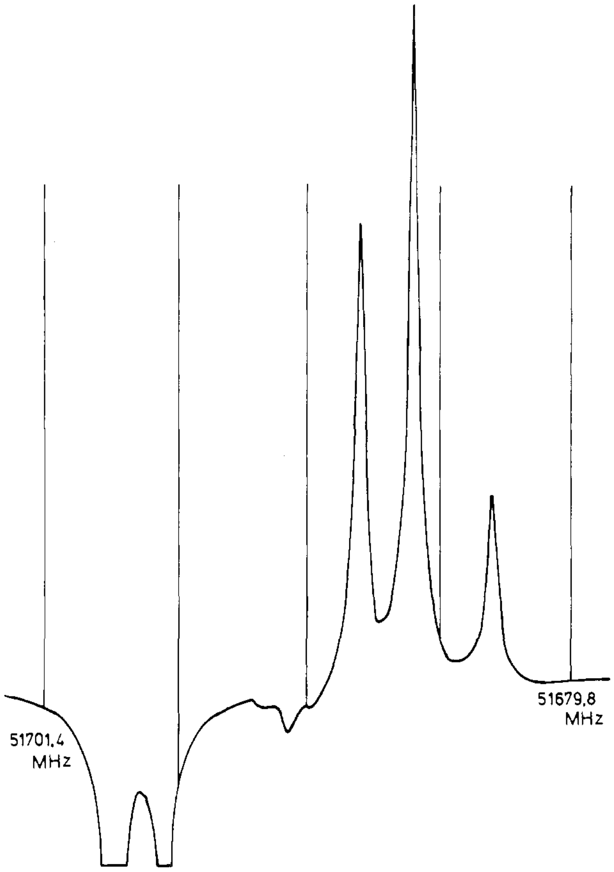

Figure 1. The 0_{00}–1_{01} μ_a transition in H_2NF. Stark field, 1300 V/cm; pressure, 3 mTorr; tc, 300 ms. Frequency markers 5.4 MHz apart.

The A rotational constant, however, depends critically on the position of the hydrogen atoms, thus, due to the uncertainty in A and the inversion splitting, the μ_c spectrum is much more difficult to predict. The initial part of this investigation, therefore, was the search for and eventual identification of the μ_a spectrum of different isotopomers of monofluoramine.

The μ_a Spectrum. The identification of the spectrum, and thus the proof of the presence of monofluoramine in the cell, started off by locating the 0_{00}–1_{01} transition with its characteristic quadrupole hyperfine structure around 51.7 GHz (Figure 1).

Since at the beginning of this investigation no microwave source with frequencies above 94 GHz was available to us, B and C had to be determined from the identification of the ${}^qQ_1(J = 4, 5, 6)$ transitions, which model calculations had shown to possess frequencies close to $J(J + 1)(B - C)/2$ as well as characteristic hyperfine structures. Eventually ${}^qQ_2$ transitions were also identified, and toward the end of the investigation, as a microwave source for the frequency range around 100 GHz arrived, the 1–2 R-branch transitions were finally measured to check the assignment and the derived rotational constants. In none of these lines was any sign of inversion splitting observed.

The investigation of the deuteriated species proceeded parallel to the investigation of the fully protonated species, except that for D_2NF the 1–2 transitions appeared within the available frequency range, appreciably facilitating the assignment of this spectrum.

Preliminary values for the quadrupole coupling constants could be determined from the μ_a spectrum alone since the 0_{00}–1_{01} transition only depends on χ_{aa} and the hyperfine structure of the higher J ${}^qQ_1$ transitions virtually only depends on $\chi^- = \chi_{bb} - \chi_{cc}$. For the final determination of the quadrupole coupling constants, however, low J μ_a as well as μ_c lines were used (see below).

The 0–1 and 1–2 transitions of $H_2{}^{15}NF$ in natural abundance (0.37%) have also been detected, as have a few rotational transitions belonging to the $v_4 = 1$ (ν_{NF}) state. A systematic search

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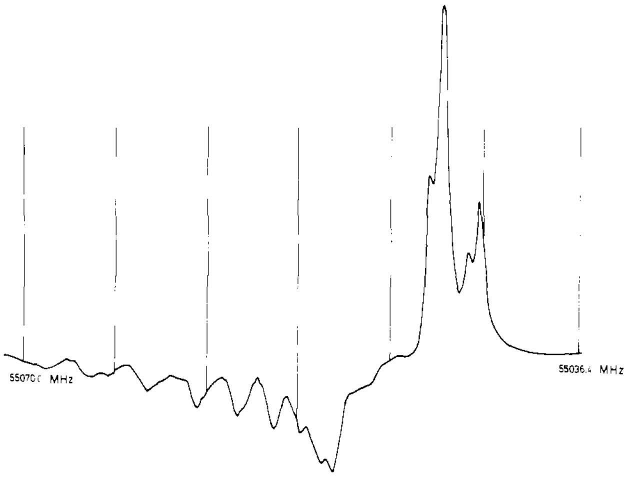

Figure 2. The 12_{111}–11_{29} μ_c transition in H_2NF. Stark field, 2080 V/cm; pressure, 3 mTorr, tc, 300 ms. Frequency markers 5.6 MHz apart.

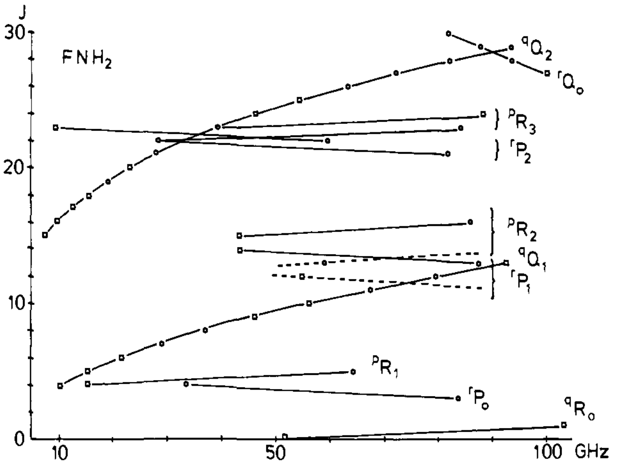

Figure 3. FORTRAT Diagram for H_2NF for $J \leq 30$ and frequencies between 7 and 105 GHz: (○) calculated, (□) measured transitions.

for these weak lines was not attempted, however.

The μ_c-Type Spectrum. The search for the μ_c-type spectrum was supported by the use of a better model, based on the analysis of the μ_a spectra. μ_a transitions with higher K_a depend weakly on A and determine this rotational constant to within 4–500 MHz. A fitting of structural parameters to the B and C rotational constants of 3 isotopic species also led to A rotational constants consistent with the high K_a transitions. One big question mark remained, however: the inversion splitting.

The search was concentrated on a region between 50 and 59 GHz, where a few, well-isolated lines were found, and the 12_{111}–11_{29} transition was identified on grounds of quadrupole hyperfine structure and Stark effect. The inversion splitting showed the 3:1 intensity relation, and the splitting itself was only 2.28 MHz (Figure 2). The assignment was checked by locating the 4_{13}–5_{05} transition at 15.76 GHz with partly resolved hyperfine structure and an inversion splitting of 2.40 MHz. The μ_c spectrum of HDNF was assigned in a similar way, but again the case of D_2NF proved much easier, because the 1_{10}–2_{02} transition with a very characteristic hyperfine structure was located in a region that had already been recorded during the search for the μ_a lines and could easily be picked out, once the general magnitude of A was known.

No inversion splitting was observed in any of the deuteriated lines. The measured transitions (corrected for quadrupole coupling effects) have been indicated in a FORTRAT diagram (Figure 3) and have been deposited as supplementary material with this journal as well as the Abteilung Strukturdokumentation, Universität Ulm, FRG.

Nuclear Quadrupole Interaction. Monofluoramine contains one nitrogen nucleus which gives rise to quadrupole coupling of the nuclear spin of 1 with the overall molecular rotation. The quadrupole moment of nitrogen is relatively small and the coupling can be analyzed in terms of first-order perturbation theory. Because the swing of the inertial axes (A,C) is too small, quadrupole coupling constants can only be determined in the molecular principal axis system. The hyperfine components of the well-resolved lines are indicated in the deposited material and the quadrupole coupling constants are collected in Table I together with those of other fluorinated amines.

Table I. Quadrupole Coupling Constants (MHz) in Fluorinated Amines (Quadrupole Principal Axis System)

	NH_3[a]	FNH_2[b]	F_2NH[c]	F_3N[d]
χ_{zz}[e]	−4.084	−6.55[f]	−8.9	−7.07
χ_{yy}	2.042	7.16	6.4	3.535
χ_{xx}	2.042	−0.61	2.5	3.535
η	0	0.83	0.44	0

[a] Reference 12. [b] This work. [c] Reference 13. [d] Reference 14. [e] Direction of lone pair. [f] See Discussion.

Centrifugal Distortion Analysis. Because of the very small inversion splitting, 0^+ and 0^- lines cannot be resolved and are treated as originating from the same state, using the average of the two μ_c components for the fitting of rotational and centrifugal distortion constants in the Watson A-reduction Hamiltonian,[15] including centrifugal distortion only to the fourth power in angular momentum. It is obvious that higher J lines with $K_a \geq 3$ cannot be fitted with this model, but for lack of more high J lines in the available frequency region, especially for the protonated species, no attempt was made to use S-reduction[15] or to include sextic centrifugal distortion constants, and instead, the few high K_a lines were omitted from the fit. The resulting rotational constants are collected in Table II.

Molecular Structure. The correct way to determine the structure of monofluoramine would be to do a lam calculation, enlarging the inertial tensor in the rotational part of the vibration–rotation Hamiltonian with the inverse G-matrix element for the inversion.[16] In the case of FNH_2, though, the inversion splitting is so small (and the barrier so high) that the molecule is virtually a rigid rotor. Thus the structure was determined as for rigid molecules.[17] The change in the NH–ND bond length is too big to be neglected in the fit. Fits with estimated changes variing between 0.2 and 0.3 pm yielded a minimum in the standard deviation for Δr(NH–ND) = 0.25 pm. The values for the structural parameters (r_0) have been collected in Table III.

In order to compensate for the harmonic vibrational contributions to the rotational constants, B_z–B_0 were calculated from the preliminary harmonic force field for FNH_2,[18] and structural parameters were fitted to these corrected rotational constants. The r_z structure is also shown in Table IV, as is the result of an ab initio MP2/6-31G** calculation.[19]

Dipole Moment. Quantitative Stark effect studies were made on a selection of μ_a and μ_c transitions of FNH_2. The voltmeter of the square-wave generator was calibrated against the 1–2 transition of OCS (dipole moment = 0.71519 D[20]) with the absorption cell at room temperature. The Stark effect is complicated due to the interaction of the quadrupole moment with the static electric field, but the transitions selected can (at the voltages applied) be described as being high-field cases (see, e.g., ref 21). Observed Stark shifts are given in Table IV as is the resulting dipole moment.

Barrier to Inversion. The very small inversion splitting shows the barrier to inversion to be high.

In order to quantify this qualitative statement, however, one must choose a model for the description of the inversion. By the

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Table II. Rotational and Centrifugal Distortion Constants (MHz) in Monofluoramine

	H_2NF	HDNF	D_2NF	$H_2{}^{15}NF$
A	263271.534 (246)	183874.375 (186)	138257.663 (152)	262385.38 (*a*)
B	26357.357 (17)	24902.416 (19)	23501.706 (21)	25601.867 (25)
C	25329.428 (17)	23301.021 (20)	21780.703 (20)	24638.721 (25)
Δ_J	0.08268 (5)	0.06692 (8)	0.05570 (16)	0.0827 (*a*)
Δ_{JK}	0.93766 (91)	0.73478 (110)	0.54359 (174)	0.9377 (*a*)
Δ_K	9.05798 (3551)	4.55786 (2996)	1.82325 (2540)	9.06 (*a*)
∂_J	0.003711 (2)	0.004607 (3)	0.004323 (10)	0.00371 (*a*)
∂_K	0.62345 (74)	0.38855 (89)	0.39202 (105)	0.6235 (*a*)
no. of lines	21	23	23	4
σ	0.120	0.123	0.144	0.168

[a] Fixed.

Table III. Structure of Monofluoramine (pm, deg) and Harmonic Corrections of Rotational Constants (MHz)

	r_0	r_z	ab initio[a]
r_{NF}	143.29 (3)	143.55 (1)	143.47
r_{NH}	102.25 (3)	102.74 (1)	101.94
∠HNF	101.08 (7)	100.88 (2)	100.95
∠HNH	106.27 (8)	105.50 (3)	104.71
	harmonic corrections[b]		
	$A_z - A_0$	$B_z - B_0$	$C_z - C_0$
FNH_2	-2541.660	-107.747	-75.156
FNHD	-1648.203	-106.960	-62.189
FND_2	-1096.659	-97.628	-57.192

[a] Reference 19 [b] Reference 18.

Table IV. Stark Shifts (MHz) and Dipole Moment (Debye) for Monofluoramine

	520 V/cm	780 V/cm	1040 V/cm	1300 V/cm	2080 V/cm
$0_{00}1_{01}$					
$M = 0$		4.97	8.39	13.42	
$1_{11}2_{12}$					
$M = 1$	26.66	56.04	94.37		
$1_{01}2_{02}$					
$M = 0$				-6.00	
$1_{10}2_{11}$					
$M = 1$		-54.16	-95.99		
$12_{111}11_{29}$					
$M = 0 + 1$					6.58
$M = 2$				2.62	7.27
$M = 3$				3.32	8.53
$M = 4$				4.07	10.17
$M = 5$				4.83	12.43
$M = 6$				5.71	14.92
$M = 7$				6.82	17.92
$M = 8$				8.01	20.77
$M = 9$				9.21	24.11
$M = 10$					28.46
$M = 11$					33.12

$\mu_a = 1.58$ (10); $\mu_c = 1.63$ (15); $\mu_t = 2.27$ (18)

elucidation of the rotational constants and structural parameters, we chose the rigid approach because of the high barrier. So for this reason, and because of lack of sufficient vibrational data, we shall also choose the simplest approach here.

For the double minimum potential we assume a simple harmonic oscillator potential perturbed by a Gaussian hump

$$V(Q) = (1/2)Q^2\lambda + A \exp(-a^2Q^2)$$

where Q is a mass-weighted displacement coordinate describing the inversion motion. This problem has been analyzed by Coon, Naugle, and McKenzie,[22] and we shall roughly follow their approach.

Assuming $\rho \equiv \ln (2Aa^2/\lambda) = 0.6$ (the value which gave the best fit for NH_3/ND_3[22]) one needs two pieces of information to construct the potential of the assumed form. One is the 0^+–0^- splitting found in this work, $G(0^-) - G(0^+) = 1.14$ MHz$/c = 3.8\ 10^{-5}$ cm^{-1}, and another is the fundamental frequency of the "inversion"–vibration, $G(1^+) - G(0^+) = 1233$ cm^{-1}.[18]

From the ratio $(G(1^+) - G(0^+))/(G(0^-) - G(0^+)) = 1233/3.8 \times 10^{-5} = 3.245 \times 10^7$, a comparison with the table Ia[22] for $\rho = 0.6$ will in principle yield $B \equiv (V(0) - V(Q_m))/(hc\nu_0)$, and $\nu_0 \equiv \sqrt{\lambda}/(2\pi c)$ can be calculated by using the measured fundamental frequency and the tabulated reduced eigenvalues.[22] This approach, however, is hampered by the very small inversion splitting in FNH_2, which requires reduced eigenvalue differences in the order of 10^{-7}. We could fit an exponential function to $(G(0^-)/\nu_0 - G(0^+)/\nu_0)$ for B between 0 and 2: $1.23631 \exp(-3.338B)$ ($r^2 = 0.9945$), which was therefore used for the extrapolation of the reduced eigenvalues leading to $B = 5.2$ and $\nu_0 = 1010$ cm^{-1}.

Thus the barrier height is 5250 cm^{-1} or 15 kcal/mol. With all these approximations and assumptions one is craving a check on these numbers. Fortunately, this is possible, albeit incorporating a further set of approximations.

The minimum in the potential is given by

$$Q_m{}^2 = \rho/a^2 = (2\rho hB)/((e^\rho - \rho - 1)4\pi^2 c\nu_0)$$

which (with the knowledge of ρ, B, and ν_0) can now be calculated. This minimum must roughly correspond to the deviation from planarity (or linearity of the NH_2 bisector) referred to the NF bond, which can be calculated from the derived r_0 structure to be 71.3°.

The relation between the deviation from planarity, γ, and Q_m is approximately

$$\gamma = Q_m/(\mu^{1/2}r_{NF})$$

where μ (the reduced mass for the inversion) can be calculated as for small out-of-plane displacements.[23]

Taking the r_{NF}, r_{NH}, and ∠HNH values from the r_0 structure, one obtains

$$\mu = 4.6697 \times 10^{-25}\ \mathrm{g}$$

and

$$Q_m = 1.248 \times 10^{-20}\ \mathrm{g}^{1/2}\ \mathrm{cm}$$

Thus

$$\gamma = 1.2743\ \mathrm{rad} = 73°$$

in fair agreement with the structural value.

An extrapolation to the 1^- and 1^+ states using the derived parameters yields a splitting of approximately 0.13 cm^{-1}. Thus high-resolution IR spectroscopy around 1230 cm^{-1} will yield further information on the shape of the inversion potential.

Discussion

The analysis of the rotational spectrum of monofluoramine now permits a complete comparison of the structural parameters of

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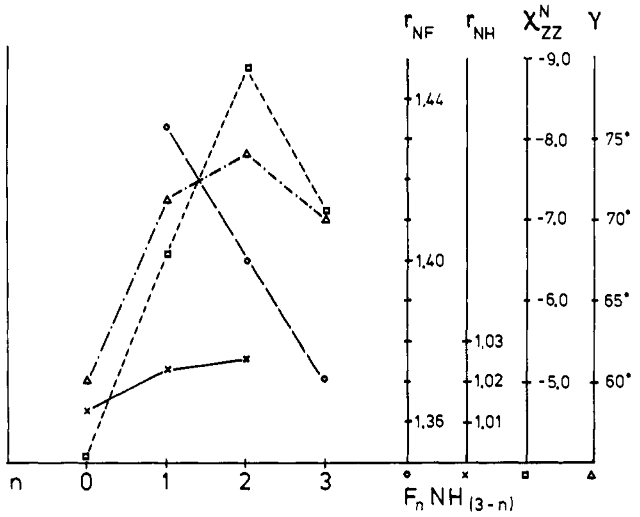

Figure 4. The variation of NF bond length in Å (○), NH bond length in Å (×), quadrupole coupling constant χ_{zz} in MHz (□), and deviation from planarity in deg (△) between ammonia and fluorinated amines.

Table V. r_0 Structures (pm, deg) of $F_nNH_{(3-n)}$ Compounds (n = 0, 1, 2, 3)

	NH_3[a]	FNH_2[b]	F_2NH[c]	F_3N[d]
r_{NF}		143.3	140.0	137.1
r_{NH}	101.4	102.3	102.6	
∠FNF			102.9	102.4
∠FNH		101.08	99.8	
∠HNH	107.3	103.3		
φ_{MEAN}	107.3	103.3	100.8	102.4
γ[e]	60.1	71.3	74.2	70.0

[a] Reference 12. [b] This work. [c] Reference 13. [d] Reference 14. [e] Angle between NX_2 bisector and NY bond.

fluorinated amines. The most obvious feature (as seen in Table V and Figure 4) is the drastic shortening of the NF bond length from 143.3 pm in monofluoramine via 140.0 pm in difluoramine to 137.1 pm in trifluoramine. This shortening is accompanied by a, much less pronounced, lengthening of the NH bond. Both of these changes can be understood in terms of polar effects, keeping in mind that the partial charge of the central nitrogen will gradually change from negative in ammonia to positive in trifluoramine, thus reversing the sign of the coulomb interactions. Hybridization does not seem to play a significant role in this change. This effect is more likely to show up in the bond angles and the quadrupole coupling constants, which, as shown in Figure 4, change in a similar, but nonlinear, way with fluorination.

The change in bond angles is best appreciated when the angle γ between the XNX bisector and the NY bond, or through the mean bonding angle, φ_{MEAN}, is used. From the change in these angles, it is obvious that the bonding orbitals acquire more p character (and the lone pair orbital thus more s character) with fluorination, except that in the C_{3v} molecule F_3N, this trend is reversed.

Table VI. Barriers to Inversion and Deviation from Planarity in H_2N-X Compounds

compound	γ (deg)	H (cm^{-1})
H_2N-CN[a]	37.96	510.1
H_2N-Ph[b]	39.35	526
H_2N-CH_3[c]	51.8	1686
H_2N-H[d]	60	1806
H_2N-OH[e]	61.71	[h]
H_2N-Cl[f]	66	4000
H_2N-F[g]	71.32	5200

[a] Reference 2. [b] Reference 24. [c] Reference 25. [d] Reference 16. [e] Reference 3. [f] Reference 7. [g] This work. [h] No inversion splitting observed.

It is difficult to be explicit about the quadrupole coupling constants in FNH_2 because only the components in the inertial axis system have been determined. If one, however, assumes the lone pair in monofluoramine to be tilted away from the external bisector at N toward the fluorine nucleus by an amount similar to that in F_2NH,[13] then the quadrupolar principal z axis is almost parallel to the inertial C axis, and, without introducing gross errors, one can assume the inertial coupling constants to be principal ones. This conclusion is reinforced by the ab initio calculations, which yields coupling constants virtually identical with the inertial constants determined here.[19]

Increased fluorination increases the barrier heights, and one can speculate whether there is a connection between the effective charge on the substituent (i.e., the polarity of the NY bond) and barrier heights, since strongly electronegative substituents will increase the p character of the bonds and thus increase the deviation from planarity, whereas substituents with a positive partial charge will increase the s character of the bonds (sp^3–sp^2) and thus lower the barrier and decrease the deviation from planarity. The data collected in Table VI seem to confirm this hypothesis, bearing in mind that occasionally other factors, like internal hydrogen bonding or interaction with an aromatic π system, may also play an important role.

Conclusion

We have succeeded in recording the microwave spectra of monofluoramine with its deuteriated isotopomers as well as a few lines of ^{15}N monofluoramine. The μ_a lines showed no sign of inversion splitting, but the μ_c lines of the protonated species were split by 2.28 MHz, leading to an inversion barrier of approximately 15 kcal/mol. Structural and quadrupole coupling parameters have been derived and compared to equivalent parameters in ammonia and fluorinated amines, showing the effects of successive fluorination of ammonia.

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Supplementary Material Available: Listing of measured (and hypothetical center) frequencies for the isotopic species H_2NF, HDNF, D_2NF, and $H_2{}^{15}NF$ (3 pages). Ordering information is given on any current masthead page.