

Figure 5. Plot of C_2^0 versus $\Theta_{4,5,6}$ (and F-Xe-F bond angle) for different $\Theta_{1,2,3}$ values (48° —, 50° --, 52° ..., 54.7° -.-). (O) represents the position of XeF₆ if it is perfectly octahedral. (The F-Xe-F angles are 90° and Θ_{1-6} is 54.7°.) In the case of $\Theta_{1,2,3}$ being 50°, the errors on C_2^0 and $\Theta_{4,5,6}$ are given by the dimensions of the box.

Finally, it is interesting to note that our C_2^0 value is much larger than that expected from the known solid-state structure.¹³ A C_2^0 value for the solid-state structure (-0.008 eV in Table II) can be estimated readily using the Mössbauer e^2qQ values in the solid state^{38,61} and using the known proportionality of C_2^0 and e^2qQ :²⁸

$$\frac{(e^2qQ)_{\text{XeF}_6}}{(e^2qQ)_{\text{XeF}_2}} = \frac{(C_2^0)_{\text{XeF}_6}}{(C_2^0)_{\text{XeF}_2}} \quad (6)$$

Using the e^2qQ values for XeF₂ and XeF₆ of +39.7 and ±7.7 mm s⁻¹, and the C_2^0 value of XeF₂, the C_2^0 value of ±0.008 eV can be readily calculated. This smaller C_2^0 value for the solid-state structure is consistent with the smaller (and different) distortion of XeF₆ in the solid state.

Conclusions

We have resolved ligand field splittings by photoelectron spectroscopy in relatively deep core levels ($E_B > 30$ eV) for the first time. To resolve these effects, it required very high resolution not previously attained in the gas phase. The spectra have been characterized using a simple Hamiltonian involving crystal field splitting and spin-orbit splitting.

Of particular interest, we have estimated the gas-phase structure of XeF₆ from the Xe 4d spectra using an additive model similar to that used in Mössbauer spectroscopy. It has been shown that for a C_{3v} XeF₆ structure, $\Theta_{1,2,3} = 50^\circ$ and $\Theta_{4,5,6} = 76 \pm 4^\circ$. This is perhaps the best experimental evidence of the distortion of gas-phase XeF₆, and it is shown to be in excellent agreement with the recent calculations of Klobukowski et al.²¹

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Registry No. XeF₂, 13709-36-9; XeF₄, 13709-61-0; XeF₆, 13693-09-9; Xe, 7440-63-3; F₂, 7782-41-4.

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An Unusual Relationship between the N-F Bond Lengths and Force Constants in N-Fluoroamines

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Abstract: The gas-phase structure of fluorodimethylamine, Me₂NF, has been studied by electron diffraction and microwave spectroscopy. A joint analysis of diffraction intensities and rotational constants results in the following skeletal geometric parameters (r_z values with 3 σ uncertainties): N-F = 1.447 (6) Å, N-C = 1.462 (7) Å, $\angle\text{CNC} = 112.0$ (10)°, and $\angle\text{FCN} = 103.6$ (5)°. The N-F bond lengths in the series Me_nNF_{3-n} increase strongly from 1.371 (2) Å in NF₃ to 1.447 (6) Å in Me₂NF. Attempts to derive clear-cut N-F force constants for the fluoromethylamines MeNF₂ and Me₂NF from vibrational frequencies failed. Ab initio calculations at the MP2/6-31G** level reproduce the experimental N-F bond lengths and the vibrational frequencies of this series very well. The calculated N-F force constants increase with increasing bond lengths from 4.58 mdyne Å⁻¹ in NF₃ to 4.77 mdyne Å⁻¹ in Me₂NF. An explanation of this unusual bond length-force constant relationship on the basis of polar effects is proposed.

Introduction

There exists no obvious a priori reason for any correlation between the length and the force constant of a certain bond. The length is determined by the position and the force constant by the

curvature of the potential minimum. Nevertheless, an inverse relation between these two quantities is widely assumed and several empirical expressions have been proposed on the basis of experimental data. Badger² suggested the relation $f = [a(r - b)]^{-1/3}$

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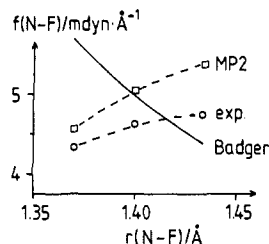


Figure 1. N-F force constants from experiment, MP2/6-31G** calculations, and Badger's rule vs experimental bond lengths in the series H_nNF_{3-n} with $n = 0-2$.

with a and b depending on the two atoms involved. A more refined expression with $f \sim r^{-3/8}$, which also takes polar effects into account, was proposed by Gordy.³ An exception to this inverse relationship has recently been pointed out for the N-F bonds in the series H_nNF_{3-n} with $n = 0-2$.⁴ For molecules of this size it is possible to derive a complete and unique force field from vibrational data and centrifugal distortion constants obtained from microwave spectra (MW). The N-F force constants increase with increasing bond lengths in going from NF_3 (N-F = 1.371 (2) Å) to H_2NF (N-F = 1.4355 (1) Å). This unusual relationship between bond lengths and force constants which is reproduced correctly by ab initio calculations at the MP2/6-31G** level is shown in Figure 1. The bond lengthening can be rationalized qualitatively by electrostatic effects. The Mulliken atomic charges indicate strong attractive $N^{\delta+}-F^{\delta-}$ interaction in NF_3 , weak attraction in HNF_2 , and repulsive electrostatic interaction $N^{\delta-}-F^{\delta-}$ in H_2NF . If this simple electrostatic model is applicable also for the methylfluoroamines Me_nNF_{3-n} , a still larger variation of the N-F bond lengths should occur in this series. Due to the strong electron-donating property of the methyl groups the negative charge at nitrogen will be higher in Me_2NF compared to H_2NF , resulting in a stronger electrostatic repulsion and in a longer N-F bond in the methyl derivative. The gas-phase structure of $MeNF_2$ has been determined by MW,⁷ but so far no structural study of Me_2NF has been reported. A novel fluorination technique⁸ allows the convenient preparation of dimethylfluoroamine in quantities required for a structure investigation in the gas phase. For this compound neither electron diffraction (ED) nor MW spectroscopy by itself can provide an accurate geometric structure. In ED high correlations between the rather similar skeletal bond lengths and bond angles and in MW the lack of stable fluorine isotopes prevent an accurate structure determination. Therefore, the structure was determined by a joint analysis of ED and MW data.

In addition to these experimental studies, we performed ab initio calculations at the MP2/6-31G** level for $MeNF_2$ and Me_2NF , using the GAUSSIAN 86 program package.⁹ This computational method was shown to reproduce the experimental geometries of the H_nNF_{3-n} series very well⁴ and also the trend of the N-F force constants (see Figure 1). The results of the calculations are listed below together with the respective experimental values.

Experimental Section

Fluorodimethylamine, Me_2NF , was prepared by fluorination of Me_2NH with NF_3O^8 at $-22^\circ C$ and purified by trap-to-trap distillation. The sample was transported from Idaho to Tübingen at liquid nitrogen temperature. Its purity was checked by ^{19}F NMR and by gas-phase IR spectra. The latter were recorded before and after the ED experiment

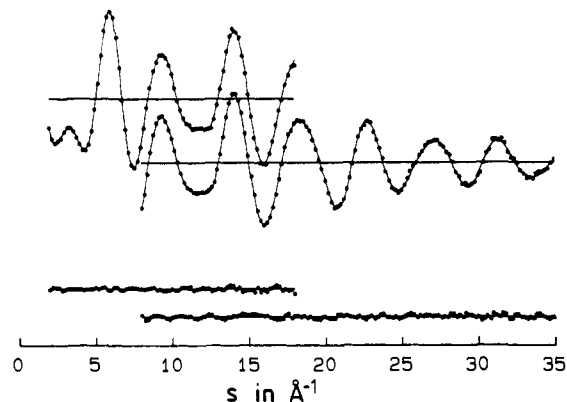


Figure 2. Experimental (dots) and calculated (full line) molecular intensities and differences for Me_2NF .

with a Perkin-Elmer 180 spectrometer in the range $200-4000\text{ cm}^{-1}$. A 10-cm KJ cell was filled under conditions equivalent to the ED experiment (see below).

ED intensities were recorded with a Balzers Gasdiffractograph¹⁰ at two camera distances (25 and 50 cm) using an accelerating voltage of ca. 60 kV. The electron wavelength was determined from ZnO diffraction patterns. The sample reservoir was kept at $-40^\circ C$, and inlet system and nozzle were maintained at room temperature. The camera pressure during the experiment did not exceed 2×10^{-5} mbar. Three plates for each camera distance were analyzed with the usual procedures.¹¹ Numerical values for the total scattering intensities are available as supplementary material and averaged molecular intensities in the s -ranges 2-18 and 8-35 \AA^{-1} in steps of $\Delta s = 0.2\text{ \AA}^{-1}$ are presented in Figure 2.

The MW spectrum was recorded in the frequency range 14-37 GHz with a conventional Stark spectrometer and a modulation frequency of 50 kHz. The absorption cell was cooled to $-50^\circ C$, and the pressure in the cell was ca. 0.02-0.03 mbar. It took a few days to condition the cell, but afterwards the compound was quite stable and only had to be exchanged in periods of several hours. Many lines not belonging to the rotational spectrum of Me_2NF were observed, though, occasionally overlapping various components of the hyperfine structure of the desired rotational transition. Me_2NF is a near oblate rotor with the c axis oriented in the direction of the nitrogen lone pair and the a axis perpendicular to the plane of symmetry. Thus, μ_b and μ_c transitions were observed, with the μ_b transitions being much stronger than the μ_c transitions. The assignment was facilitated by the use of rotational constants calculated for the preliminary ED structure.

The $0_{00}-1_{11}$ transition was sought and identified by means of its characteristic quadrupole hyperfine structure and its Stark effect. The search for the $0_{00}-1_{10}$ transition was much more difficult because of the weakness of this transition, but the assignment of these two transitions immediately determined the quadrupole coupling constants of Me_2NF . Afterwards the assignment of the spectrum was quite straightforward. 10 R-branch and 55 Q-branch transitions ($5 \leq J \leq 29$) were eventually assigned and measured. The hypothetical centerfrequencies ν_0 were fit to a quartic Watson-type Hamiltonian in the IR representation. Because of the oblateness of this molecule, a calculation was also performed in the IIII representation, but this did not alter the quality of the fit. The measured R-branch transitions are collected in Table I together with rotational and centrifugal distortion as well as quadrupole coupling constants. The Q-branch transitions are available as supplementary material and have been deposited at "Strukturdokumentation, University of Ulm, Germany".

Force Fields of $MeNF_2$ and Me_2NF

The IR spectra of both compounds are readily assigned with the help of the ab initio values for vibrational frequencies and their intensities. Several attempts were made to derive valence force constants from the experimental vibrational frequencies of $MeNF_2$ ¹² and Me_2NF (Table II), using the program NORCOR.¹³ Normal coordinate analyses demonstrate that strong couplings

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Table I. Observed R-Branch Transitions (MHz), Experimental and Calculated Rotational Constants (MHz), Centrifugal Distortion Constants (kHz), and Quadrupole Coupling Constants (MHz) for Me₂NF

J'	K'₋	K'₊	J''	K''₋	K''₊	F'	F''	ν _{obs}	ν _o	ν _o - ν _{calc}	
1	1	1	0	0	0	2	1	14 451.36	14 451.72	0.14	
						1	1	14 453.41			
						0	1	a			
1	1	0	0	0	0	1	1	18 269.38	18 271.02	-0.05	
						2	1	18 271.37			
						0	1	18 274.41			
2	1	2	1	0	1	1	0	24 790.64	24 792.35	-0.06	
						3	2	24 791.86			
						2	1	24 794.11			
2	2	1	1	1	0	1	0	33 010.12	33 013.47	-0.07	
						3	2	33 013.12			
						2	1	33 015.15			
2	0	2	1	1	1	1	1	24 482.00	24 485.28	0.01	
						3	2	24 485.13			
						2	1				
						1	0				
						2	2	24 787.14			
2	1	1	1	0	1	2	1	36 249.21	36 250.86	0.05	
						3	2	36 251.30			
						1	0	36 252.58			
2	2	0	1	1	0	1	0	36 555.90	36 557.84	-0.04	
						2	2				
						3	2	36 557.97			
						2	1				
						1	1	36 561.33			
						2	1	36 831.39	36 833.08	0.04	
2	2	1	1	1	1	1	1				
						3	2	36 833.45			
						2	2				
						1	0	36 836.43			
3	1	3	2	0	2			b	34 993.75	0.00	
3	0	3	2	1	2			b	34 977.20	0.02	
			<i>B</i> ' _o (exp)			<i>B</i> ' _z (exp)			<i>B</i> ' _z (calc)		
A			9281.12 (2)			9274.5 (10)			9274.8		
B			8990.00 (2)			8979.7 (15)			8978.7		
C			5170.48 (2)			5168.8 (3)			5168.6		
Δ _J = 7.0 (15)			Δ _{JK} = 0.3 (3)			Δ _K = 5.3 (3)			δ _J = 1.6 (1)		
			χ _{aa} = 0.11			χ _{bb} = 6.71			χ _{cc} = -6.82		

^aOverlap. ^bHyperfine structure not resolved.

Table II. Experimental and Scaled (See Text) Theoretical (MP2/6-31G**) Vibrational Frequencies (cm⁻¹) and Intensities (in Brackets) for Me₂NF

A'			A''		
IR gas	MP2/6-31G**		IR gas	MP2/6-31G**	
ν ₁	3010 m	3008 (10)	ν ₁₄	3010 m	3007 (11)
ν ₂	2970 vs	2967 (33)	ν ₁₅	2970 vw	2964 (1)
ν ₃	2870 vs	2869 (39)	ν ₁₆	2870 s	2866 (17)
ν ₄	1475 s	1482 (13)	ν ₁₇	n.o. ^a	1462 (0.1)
ν ₅	1449 m	1450 (6)	ν ₁₈	1440 m	1438 (9)
ν ₆	1415 w	1412 (3)	ν ₁₉	n.o.	1391 (0.04)
ν ₇	1190 m	1193 (6)	ν ₂₀	1200 w	1213 (1)
ν ₈	1160 w	1163 (3)	ν ₂₁	1090 w	1074 (2)
ν ₉	930 s	932 (14)	ν ₂₂	985 w	975 (5)
ν ₁₀	785 vs	801 (27)	ν ₂₃	435 w	415 (5)
ν ₁₁	465 w	480 (3)	ν ₂₄	n.o.	245 (0.2)
ν ₁₂	410 w	406 (4)			
ν ₁₃	n.o.	304 (0.4)			

^aNot observed.

between various internal coordinates occur in these two molecules which lead to large interaction force constants. The experimental frequencies can be reproduced almost equally well with rather different sets of force constants, all of which can be considered to be "reasonable". Therefore, it is impossible to derive clear-cut N-F force constants from the experimental frequencies of these two compounds which then can be correlated with the bond lengths. On the other hand, the ab initio calculations for the methylfluoroamines reproduce the experimental frequencies very well, if the calculated values are multiplied with three different scaling factors: 0.93 for C-H stretch, 0.94 for skeletal stretch and CH₃ deformations, and 1.00 for skeletal deformations. The

Table III. Ab Initio Values for Diagonal Skeletal Force Constants of NF₃, MeNF₂, and Me₂NF in mdyn Å⁻¹ and mdyn Å^a

	NF ₃	MeNF ₂	Me ₂ NF
N-F	4.58	4.66	4.77
N-C		5.06	5.31
FNF	2.02	2.95	
CNC			1.29
CNF		1.74	1.66

^aComplete sets of force constants can be obtained from the authors upon request.

scaled ab initio frequencies fit the experimental values with an average deviation of Δν = 9 cm⁻¹ (MeNF₂) and 7 cm⁻¹ (Me₂NF, see Table II), respectively. This close agreement of the frequencies suggests that a "unique" conventional force field can be derived by scaling the ab initio force constants so as to fit the experimental frequencies. This procedure,¹⁴ however, is hampered by the fact that in the two amines interactions between nonadjacent internal coordinates, which are normally neglected in conventional force fields, are calculated to be rather large (e.g., NF/NCH = 0.17 mdyn, FNF/NCH = -0.24 mdyn·Å in MeNF₂ and NF/NCH = 0.13 mdyn, FNC/NCH = 0.19 mdyn·Å in Me₂NF). Thus, if the scaling procedure is applied to the complete ab initio force fields, the experimental frequencies are reproduced very well, but these results do not resemble conventional experimental force fields. The meaningfulness of such large nonconventional interaction force constants is still open to debate, but in this investigation, where our main interest is the trend of the N-F force

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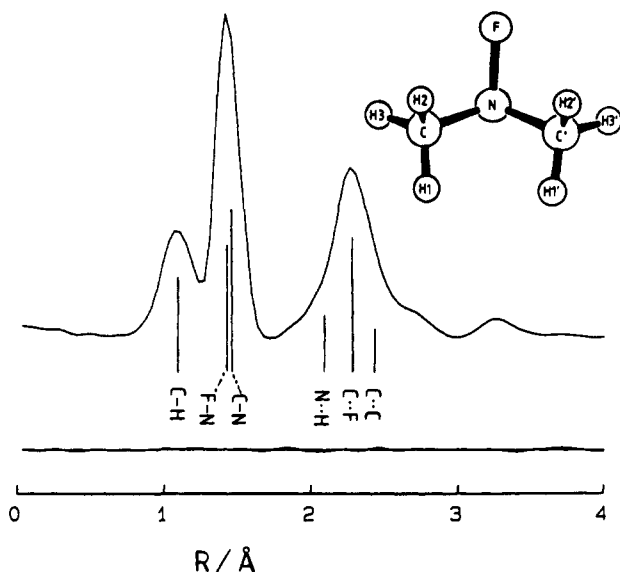


Figure 3. Experimental radial distribution function and difference curve. Positions of interatomic distances (without C...H, F...H, and H...H distances) are indicated by vertical bars.

Table IV. Results of Experimental Structure Analyses for Me_2NF^a

Geometric Parameters				
	ED (r_a values)		ED + MW (r_z values)	
N-F	1.434	(27)	1.447	(6)
N-C	1.463	(20)	1.462	(7)
C-H	1.100	(6)	1.096	(4)
CNC	112.1	(19)	112.0	(10)
FNC	104.0	(15)	103.6	(5)
HCH	110.6	(19)	110.5	(13)
δ (C'NCH) ^b	50	(4)	50	(3)

Interatomic Distances, Vibrational Amplitudes, and Harmonic Vibrational Corrections (without H...H Distances)				
distance	l (ED + MW)	l (spectr)	$\Delta r = r_a - r_z$	
C-H	1.10	0.082 (3)	0.079	+0.006
N-F	1.45	0.045 (7)	0.050	+0.001
N-C	1.46	0.053 (6)	0.050	+0.001
N...H	2.09	0.113 (18)	0.106	+0.001
F...C	2.29	0.069 (6)	0.068	-0.001
C...C	2.42	0.074 (12)	0.066	-0.001
(X...H) _{gauche} ^c	2.34-2.74	0.135 (27)	0.154-0.160	-0.001-+0.001
(X...H) _{trans}	3.23-3.36	0.094 (21)	0.106	+0.004

^a Distances in Å, angles in deg. Error limits refer to the last digit and are 3σ values. For atom numbering see Figure 3. ^b For $\delta = 60^\circ$, the methyl groups stagger exactly the opposite N-C bond. ^c X = C or F.

constants and not so much their absolute values, we shall simply correlate the unscaled ab initio values to the experimental bond lengths. The diagonal skeletal force constants for the series $\text{Me}_n\text{NF}_{3-n}$ with $n = 0-2$ are collected in Table III.

Structure Analysis for Me_2NF

A preliminary structural model was derived from the radial distribution function (Figure 3) which then was refined by a least-squares method. For this purpose the molecular intensities were multiplied with a diagonal weight matrix; scattering amplitudes and phases of Haase¹⁵ were used. C_3 overall symmetry and local C_{3v} symmetry of the methyl groups were assumed. Refinements of tilt angles between the C_3 axis of the CH_3 groups and the N-C bond direction resulted in values which were smaller than the corresponding standard deviations. Therefore, this tilt was set to zero in the further analyses. Vibrational amplitudes for nonbonded F...H and C...H distances were collected in groups

Table V. Experimental and Calculated Geometries of the Series $\text{Me}_n\text{NF}_{3-n}$

	NF_3		MeNF_2		Me_2NF	
	MW ^a	MP2 ^b	MW ^c	MP2 ^d	ED + MW ^d	MP2 ^d
N-F	1.371 (2)	1.385	1.413 (7)	1.416	1.447 (6)	1.448
N-C			1.449 (5)	1.459	1.462 (7)	1.455
FNF	102.2 (1)	101.7	101.0 (5)	101.8		
FNC			104.6 (4)	103.2	103.6 (5)	102.9
CNC					112.0 (10)	111.7

^a Reference 5. ^b Reference 4. ^c Reference 7. ^d This work.

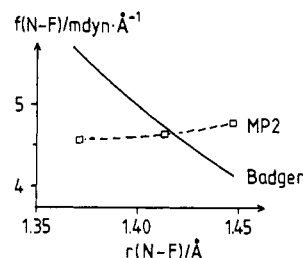


Figure 4. N-F force constants from MP2/6-31G** calculations and Badger's rule vs experimental bond lengths in the series $\text{Me}_n\text{NF}_{3-n}$ with $n = 0-2$.

according to their distances. With these assumptions seven geometric parameters and eight vibrational amplitudes were refined simultaneously. High correlations between the closely spaced N-F and N-C distances and their amplitudes lead to large standard deviations for these parameters (see Table IV).

In the next step the rotational constants were included in the structure analysis. The harmonic corrections for interatomic distances $\Delta r = r_a - r_z$ and rotational constants $\Delta B^i = B_0^i - B_z^i$ which are required for a joint analysis of ED and MW data were calculated from an experimental valence force field.¹⁶ The contributions of the methyl torsional vibrations to the corrections Δr were neglected for the torsion-independent distances (C-H, N...H, and H...H within CH_3 groups), because the concept of perpendicular vibrations makes the calculated contributions unrealistically large for these distances.¹⁷ The corrections Δr are given in Table IV, and the corrected rotational constants B_z^i are included in Table I. The uncertainties of B_z^i are estimated to be 15% of the corrections ΔB^i . The relative weight of ED and MW data was adjusted so as to fit the rotational constants within their estimated uncertainties (see Table I). The geometric parameters and vibrational amplitudes of the joint analysis are collected in Table IV.

Discussion

The gas-phase structure of Me_2NF could be determined by joint analysis of ED and MW data with an accuracy required for the discussion of bonding properties. The skeletal parameters of the series $\text{Me}_n\text{NF}_{3-n}$ ($n = 0-2$) are compared in Table V. The most interesting parameter is the N-F bond length which increases with stepwise substitution of F by Me from 1.371 (2) Å in NF_3 to 1.447 (6) Å in Me_2NF . This trend which is more pronounced than that in the $\text{H}_n\text{NF}_{3-n}$ series (N-F = 1.4355 (1) in H_2NF_2) is in accordance with the simple electrostatic model proposed in the Introduction. The ab initio calculations reproduce the absolute values of the N-F bond lengths as well as the trend in the force constants in the $\text{H}_n\text{NF}_{3-n}$ series very well. Since the same computational method (MP2/6-31G**) also reproduces the absolute values of the N-F bond lengths in the $\text{Me}_n\text{NF}_{3-n}$ series equally well, we are confident that the trend in the force constants in the methyl compounds is predicted correctly. In lack of reliable experimental values we therefore use these calculated force constants for correlation with the experimental bond lengths

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(Figure 4). Similar to the H_nNF_{3-n} series (Figure 1), the force constants increase with increasing bond lengths, a trend which contradicts the relation represented by Badger's rule. In search for other examples of such an opposite bond length-force constant relationships we only found one more case, i.e., the O-F bonds in OF_2 and HOF . The bond lengthens from 1.4124 Å in OF_2 ¹⁸ to 1.442 (2) Å in HOF ,¹⁹ and the force constant increases from 3.95¹⁸ to 4.418 mdyne-Å⁻¹.²⁰ In other fluorine derivatives for which the bond lengths and clear-cut force constants are known, such as H_nCF_{4-n} ⁴ or H_nPF_{3-n} ,²¹ the relationship shows normal behavior, i.e., the force constants decrease with increasing bond lengths.

A possible rationalization of this unusual property of the N-F bond is based on electrostatic effects.⁴ Assuming that the bonding potential can be regarded as a superposition of covalent and electrostatic contributions, a repulsive coulombic term lengthens the bond and increases the force constant and vice versa, provided that the covalent part of the potential remains unchanged. This model suggests that the variation of the N-F bond lengths in the hydrogen and methylfluoroamines is predominantly due to electrostatic interactions, which vary from strongly attractive in NF_3 to repulsive in H_2NF and Me_2NF , and that the covalent con-

tribution remains nearly constant. On the other hand, lengthening of C-F and P-F bonds can be rationalized as being partly due to electrostatic effects and partly due to lowering of the covalent bond strength. In this case, the increase of the force constant due to electrostatic effects is overcompensated by simultaneous decrease of the covalent contribution. Thus, the force constants show normal behavior, i.e., they decrease with increasing bond lengths, but this decrease is less than that predicted by Badger's rule.

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Note Added in Proof. After submission of this paper a reinvestigation of the gas-phase structure of $MeNF_2$ using electron diffraction intensities and rotational constants was initiated by K. Hagen, K. Hedberg, E. O. John, R. Kirchmeier and J. M. Shreeve. The preliminary results indicate that the N-F bond length given in Table V of this paper remains unchanged within its error limit and the N-C bond is slightly longer than the value derived from rotational constants only.

Supplementary Material Available: Total electron diffraction intensities and Q-branch rotational transitions for Me_2NF (6 pages). Ordering information is given on any current masthead page.

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Coherence Transfer in Nuclear Magnetic Resonance by Selective Homonuclear Hartmann-Hahn Correlation Spectroscopy

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Abstract: New NMR techniques are described for transferring transverse magnetization between scalar-coupled nuclei in the rotating frame. The methods involve simultaneous spin-locking of two selected spins A and X, using cosinusoidal modulation of the radio frequency (rf) carrier. If transverse magnetization of spin A is excited selectively before spin-locking, for example with a self-refocusing 270° Gaussian pulse, in-phase magnetization will be transferred from spin A to spin X, and in-phase multiplets are obtained in both one- and two-dimensional spectra. The method allows one to verify whether two particular spins are connected by a scalar coupling. Examples are shown for peptides and basic pancreatic trypsin inhibitor (BPTI). The fine structure of the multiplets yields information on couplings to further spins. In contrast to nonselective spin-lock experiments, the magnetization cannot diffuse to a manifold of coupling partners. If relayed coherence transfer is to be achieved deliberately, several spins may be locked simultaneously by imposing an additional modulation on the rf carrier.

Introduction

Much has been written¹⁻¹⁰ in recent years about the relative merits of conventional correlation spectroscopy (COSY) and total correlation spectroscopy (TOCSY), the latter being also known

as homonuclear Hartmann-Hahn spectroscopy (HOHAHA). Both methods are intended to reveal scalar couplings or networks of couplings. While COSY multiplets only reflect direct connectivities, TOCSY multiplets also appear when two spins merely belong to the same coupling network, so the latter method may be compared to relayed magnetization-transfer experiments. Generally speaking, TOCSY experiments must be regarded as more demanding from an experimental point of view, with special requirements on radio frequency (rf) power and phase coherence. Furthermore, the interpretation may be hampered if some areas in the spectra appear "bleached" because of unfavorable conditions, notably if offset effects give rise to tilted effective fields. Difficulties may also arise from cross-relaxation effects in the rotating frame (so-called ROESY effects), so a variety of methods have been developed to separate coherent and incoherent processes in spin-locking experiments.^{11,12}

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