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Structure and Vibrational Force Field of Methyldifluoroamine, CH_3NF_2. An Electron-Diffraction Investigation Augmented by Microwave and Infrared Spectroscopic Data and by Ab Initio Molecular Orbital Calculations

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The structure of methyldifluoroamine, CH_3NF_2, was determined by gas-phase electron diffraction augmented by rotational constants from microwave spectroscopy taken from the literature and by results from molecular orbital calculations. The structural results are consistent with C_s symmetry for a molecule with staggered bonds. The experimental bond distances and bond angles (r_α^0/r_g) and $\angle_\alpha$), with estimated 2σ uncertainties are C−H = 1.104/1.124(5) Å (average value), N−F = 1.406/1.408(2) Å, C−N = 1.467/1.469(6) Å, C−N−F = 104.1(2)°, F−N−F = 101.7(2)°, N−C−H_{anti} = 109.9(11)°, N−C−H_{gauche} = 106.5(10)°, H_{gauche}−C−H_{gauche} = 110.6(28)°; the subscripts indicate orientation with respect to the nitrogen lone pair. A scaled quantum-mechanical (SQM) quadratic vibrational force field was evaluated by symmetrizing the quantum-mechanical (MP2/6-311++G(d,p)) Cartesian force constants and scaling the results to fit observed infrared wavenumbers from the literature. The N−F stretching force constants for the other fluoroamines NF_3 and $(CH_3)_2NF$ were also determined in a similar fashion. Contrary to an earlier report, the values were found to increase with decreasing bond length consistent with Badger's rule.

Introduction

Ever since it was first observed in the case of fluorinated methanes[1] more than 60 years ago, the effect of increasing fluorine substitution on an atom has been known to shorten the bonds to fluorine. Thus, the length of the N−F bond is expected to increase significantly in the series of molecules $Me_nNF_{(3-n)}$ Me = CH_3; $n = 0-2$, as fluorine atoms are successively replaced by methyl groups. The experimental values—1.371(2) Å for NF_3 from microwave spectroscopy (MW),[2] 1.413(5) Å for $MeNF_2$ from MW,[3] and 1.447(6) Å for Me_2NF from combined electron diffraction (GED) and MW[4]—are consistent with the expected bond-length variation.

As a part of the Me_2NF study cited above, the relationship between the N−F bond length and the value of the stretching force constant in the $Me_nNF_{(3-n)}$ series of molecules was also investigated. The results suggest that a violation of Badger's rule occurs. Badger's rule[5] states that the bond lengths between atoms of a given type and the corresponding stretching force constants are inversely related; the formula is $k_e = a(r_e - b)^{-1/3}$, with a and b depending on the atoms involved. For the amines cited above, the N−F force constants were found to increase slightly instead of decreasing as the number of fluorine atoms changes from three to one. Because Badger's rule has enjoyed considerable success, this matter is puzzling. One aspect of the problem concerns the MW results for $MeNF_2$ which rest on some assumptions about the hydrogen parameters. Another concerns a possible ambiguity in the identification of the N−F "force constant" in this molecule, which arises from the existence of two stretching modes, a symmetric and an asymmetric one, which have different wavenumber values. This article is a report of our GED investigation of $MeNF_2$ (Figure 1), which also includes a normal coordinate analysis of the molecule, and makes auxiliary use of the earlier data from MW[3] and infrared[6] spectroscopy. Related to this work we also carried out ab initio molecular orbital calculations, some at high levels of theory, for all three $Me_nNF_{(3-n)}$ molecules. These calculations have given us important information about both their structures and their quadratic vibrational force fields.

Experimental Section

Methyldifluoroamine was prepared by photolyzing CH_3I and N_2F_4 through Pyrex using a Hanovia benchtop UV lamp[7] and was purified by trap-to-trap distillation. The electron-diffraction data were obtained with the Oregon State apparatus (nominal accelerating voltage of 60 kV) with a nozzle-tip temperature of 295 K and with the bulk sample kept at 223 K. The nozzle-to-plate distances were 748.16 and 299.34 mm for the long (LC) and the middle (MC) camera distance experiments, respectively. Exposure times were 2−3 min, beam currents were 0.39−0.45 μA, plates were Kodak projector slide, medium contrast, developed for 10 min in D19 diluted 1 × 1. The electron wavelength was 0.048721 Å. A voltage/distance calibration was made with CO_2 as reference (r_a(C−O) = 1.1646 Å; r_a(O•O) = 2.3244 Å). Three plates from the LC and two plates from the MC experiments were selected for analysis. The plates were scanned twice, making a total of 10 data sets. The ranges of data were $2.00 \leq s/\text{Å}^{-1} \leq 15.50$ and $8.00 \leq s/\text{Å}^{-1} \leq 37.00$ for the LC and MC distance experiments, respectively. The data interval was $\Delta s = 0.25$ Å^{-1}. A calculated background[8] was subtracted from each data set to yield experimental intensity

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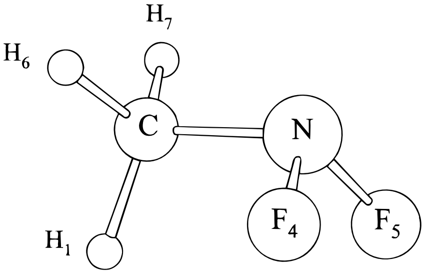

Figure 1. Diagram of the methyldifluoroamine molecule with atom numbering.

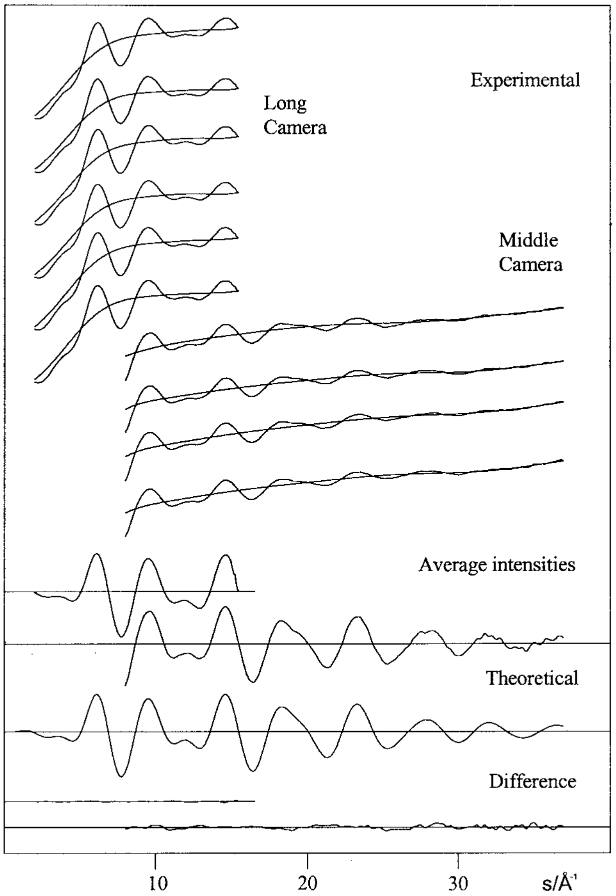

Figure 2. Intensity curves. Long camera and middle camera curves are magnified two times relative to the backgrounds on which they are superimposed. Average curves are in the form *sI$_m$(s)*. The theoretical curve is calculated from the final model shown in Tables 4 and 5. Difference curves are experimental minus theoretical.

data in the form $sI_m(s)$. The intensity curves with backgrounds are shown in Figure 2. An experimental radial distribution (RD) curve was calculated in the usual way from the modified molecular intensity curve $I'(s) = sI_m(s)Z_CZ_F(A_CA_F)^{-1} \exp(-0.002s^2)$, where $A = s^2F$ and F is the absolute value of the complex electron scattering amplitudes, using theoretical intensity data for the unobserved or uncertain region $s \leq 1.75$ Å^{-1}. The scattering amplitudes and phases (also used in subsequent calculations) were taken from tables.[9] The intensity data and final backgrounds are available as Supporting Information.

Molecular Orbital Calculations. Ab initio molecular orbital optimizations of the MeNF$_2$ structure were done with several bases at different levels of theory using the program Gaussian 94.[10] All calculations at the Hartree−Fock level gave a N−F bond length much shorter (ca 0.06 Å) than the experimental value earlier reported for this molecule.[3] Values from the MP2, MP3, and B3LYP levels were much closer, differing by only a few thousandths of an angstrom. Results for these calculations are given in Table 1. Optimizations of the NF$_3$ and Me$_2$NF structures were also carried out at a few theoretical levels (HF/6-311++G(d,p), MP2/6-311++G(d,p), and B3LYP/6-311++G-(2d,2p)), and frequencies and Cartesian force fields at these levels were calculated for all three molecules. The calculations for NF$_3$ and Me$_2$NF were for use in comparisons of force-constant values. These comparisons are discussed in a later section.

Normal Coordinate Calculations. The ab initio Cartesian force fields were used in the program ASYM40[11] to obtain symmetry force fields or valence force fields. A set of scale factors for the nonredundant set of symmetry force constants was then refined to fit the observed vibrational wavenumbers[6] for MeNF$_2$, and the resulting scaled (SQM) force field used to calculate the quantities that interconvert r_α^0 and r_a, and B_z and B_0 needed to utilize the available rotational constants and GED data simultaneously in the structure refinement.[12] Table 2 lists the symmetry coordinates for MeNF$_2$ and Table 3 lists the corresponding force constants, scale constants, and wavenumbers.

Structure Analysis

Assuming C_s symmetry for the molecule, the structure of MeNF$_2$ can be described by four distance and five angle parameters. These were chosen to be $\langle r(\mathrm{C-H})\rangle = {}^1/_2[r(\mathrm{C-H_1}) + r(\mathrm{C-H_6})]$, $\Delta r(\mathrm{C-H}) = r(\mathrm{C-H_1}) - r(\mathrm{C-H_6})$, $r(\mathrm{C-N})$, $r(\mathrm{N-F})$, $\angle(\mathrm{C-N-F})$, $\angle(\mathrm{F-N-F})$, $\angle(\mathrm{N-C-H_1})$, $\angle(\mathrm{N-C-H_6}) = \angle(\mathrm{N-C-H_7})$, and $\angle(\mathrm{H_6-C-H_7})$. There are also vibrational amplitude parameters constructed by grouping individual amplitudes together; the makeup of these is seen in the table of final results. A trial structure was constructed from the appearance of the experimental radial distribution curve and from the ab initio, MW, and ASYM40 results. Refinements of this structure, based at first on the electron diffraction data alone, were done by the method of least squares,[13] adjusting a theoretical $sI_m(s)$ curve simultaneously to the 10 experimental data sets using a unit weight matrix. It was quickly discovered that the parameters $r(\mathrm{C-N})$ and $r(\mathrm{N-F})$ were correlated strongly with the value of the vibrational amplitudes for these distances—their average could be determined accurately, but the difference between them could not. Nor could the parameter $\Delta r(\mathrm{C-H})$ be refined simultaneously with the vibrational amplitudes for the C−H bonds; it was therefore held at the MP2/6-311++G-(2d,2p) value. The refinements were next expanded by inclusion of five sets of three rotational constants B_z derived from the B_0's for the isotopic species CH$_3$NF$_2$, ^{13}CH$_3$NF$_2$, CD$_3$NF$_2$, *sym*-CDH$_2$NF$_2$, and *asym*-CDH$_2$NF$_2$,[3] taking into account the effect of the expected isotopic shifts $r(\mathrm{C-D}) - r(\mathrm{C-H})$; the weighting of the rotational constant data relative to those from GED was such as to yield a variance ratio for the final model of about 65:1 = GED:MW. The MW data comprised a set of constraints on the structure to be obtained from the GED analysis; their inclusion removed the ambiguities obtained with use of GED data alone and allowed the simultaneous refinement of eight geometric parameters and three amplitude parameters. The geometric parameter values resulting from this refinement are given in Table 4 together with values from some of the ab initio calculations and the earlier MW results. The interatomic distances and corresponding vibrational amplitudes are given in Table 5 and the fit to the rotational constants are given in Table 6. Table 7 is the correlation matrix for the refined parameters. Intensity curves for the final model are shown in

TABLE 1: Optimized Parameter Values for Methyldifluoroamine from Several Levels of Theory[a]

	HF/				MP2/			MP3/	B3LYP/			
basis	6-31G(d)	6-311++ G(d,p)	6-311++ G(2d,2p)	6-311++ G(2df,2pd)	6-31G(d)	6-311++ G(d,p)	6-311++ G(2d,2p)	6-311++ G(2d,2p)	6-31G(d)	6-311++ G(d,p)	6-311++ G(2d,2p)	6-311++ G(2df,2pd)
r(C−H$_1$)	1.0816	1.0834	1.0803	1.0812	1.0913	1.0921	1.0852	1.0851	1.0936	1.0919	1.0887	1.0893
r(C−H$_6$)	1.0797	1.0807	1.0780	1.0783	1.0899	1.0834	1.0835	1.0832	1.0919	1.0898	1.0871	1.0874
r(C−N)	1.4500	1.4515	1.4484	1.4485	1.4613	1.4608	1.4580	1.4604	1.4662	1.4644	1.4615	1.4609
r(N−F)	1.3600	1.3500	1.3527	1.3481	1.4166	1.4022	1.4112	1.3922	1.4144	1.4148	1.4154	1.4096
∠C−N−F	105.08	105.85	105.75	105.85	103.13	104.28	103.73	104.19	103.50	104.50	104.30	104.47
∠F−N−F	102.30	102.49	102.39	102.48	101.81	102.22	101.86	101.85	102.06	101.93	101.78	101.87
∠N−C−H$_1$	110.38	110.74	110.67	110.74	110.22	110.94	110.76	110.73	110.68	111.36	111.26	111.24
∠N−C−H$_6$	107.26	107.06	107.07	107.13	106.78	106.56	106.57	106.81	106.99	106.54	106.55	106.63
∠H$_6$−C−H$_7$	110.00	109.96	109.98	109.96	110.34	110.20	110.20	110.10	109.99	109.89	109.96	109.93

[a] Distances in angstroms, angles in degrees.

TABLE 2: Symmetry Coordinates for Methyldifluoroamine[a]

A′ species	A″ species
$S_1 = \Delta r_{12}$	$S_{10} = 1/\sqrt{2}\Delta(r_{26} - r_{27})$
$S_2 = 1/\sqrt{2}\Delta(r_{26} + r_{27})$	$S_{11} = 1/\sqrt{2}\Delta(r_{34} - r_{35})$
$S_3 = 1/\sqrt{2}\Delta(r_{34} + r_{35})$	$S_{12} = 1/2\Delta(\alpha_{126} - \alpha_{127} + \alpha_{326} - \alpha_{327})$
$S_4 = \Delta r_{23}$	$S_{13} = 1/2\Delta(\alpha_{126} - \alpha_{127} - \alpha_{326} + \alpha_{327})$
$S_5 = \Delta\alpha_{627}$	$S_{14} = 1/\sqrt{2}\Delta(\alpha_{234} - \alpha_{234})$
$S_6 = 1/2\Delta(\alpha_{126} + \alpha_{127} - \alpha_{326} - \alpha_{327})$	$S_{15} = 1/6\Delta(\tau_{1234} + \tau_{1235} + \tau_{6234} + \tau_{6235} + \tau_{7234} + \tau_{7235})$
$S_7 = \Delta\alpha_{123}$	
$S_8 = \Delta\alpha_{435}$	
$S_9 = 1/\sqrt{2}\Delta(\alpha_{234} + \alpha_{235})$	

[a] For atom numbering see Figure 1.

Figure 2 and the corresponding radial distribution curves are shown in Figure 3.

Discussion

Table 8 offers a comparison of the structures of several fluoroamines. Our parameter values for MeNF$_2$ differ somewhat from those obtained in the MW work. We find the N−F bond to be slightly shorter, and the C−N bond to be significantly longer. Because our structure provides a good fit to the rotational constants as well as the GED data, we feel it to be the more accurate. The phenomenon of progressive bond shortening with increasing fluorine substitution is evident. Their values in the series NF$_3$ → MeNF$_2$ → Me$_2$NF are respectively 0.035 and 0.041 Å. Similar but slightly smaller changes are seen in the series with hydrogen replacing the methyl groups:[2,14,15] for NF$_3$ → HNF$_2$ → H$_2$NF they are 0.029 and 0.033 Å. The shortening effect in X−F bonds accompanying increasing fluorine substitution has long been known. The case of the NF$_3$ → MeNF$_2$ → Me$_2$NF series has been discussed.[4]

The molecule MeNF$_2$ is small enough to make possible tests of the reliability of theoretical calculations for structural predictions. As is seen in Tables 1 and 4, none of the calculations at the HF level reproduced the correct N−F bond length: all resulted in too small values which became still smaller as the size of the basis set increased, diffuse functions were added, and polarization included. For the C−N bond and for the bond angles, the HF calculations gave results in better agreement with the experimental results, but again larger basis sets did not lead to improvement. When electron correlation was included at the MP2 level, the agreement with the experimental N−F bond length was much improved. Inclusion of electron correlation at the MP3 level, however, did not change the results very much and the agreement with the experimental N−F bond length actually worsened. It is noteworthy that all results from use of the B3LYP hybrid method, even those from a relatively small basis set, were in good agreement with the experimental results.

We have also investigated the matter of the apparent violation of Badger's rule in the NF$_3$, MeNF$_2$, and Me$_2$NF series of molecules reported earlier.[4] The apparent violation was based on results of ab initio calculations at the MP2/6-311G(d,p) level from which it seemed that the N−F stretching force constants in the series *increased* with increasing bond length instead of decreasing as predicted by the rule. As Table 3 shows, we have been able to fit the observed frequencies of MeNF$_2$[6] very well

TABLE 3: Symmetry Force Constants, Scale Factors, and Wavenumbers for Methyldifluoroamine[a]

scale factors[b]		F$_1$	F$_2$	F$_3$	F$_4$	F$_5$	F$_6$	F$_7$	F$_8$	F$_9$	assignments	ω_{obs}	ω_{calcd}
0.903(3)	F$_1$	5.499									CH str	3027.0	3039.9
0.903(3)	F$_2$	0.013	5.622				A′				CH sym str	2957.0	2942.7
0.927(11)	F$_3$	0.022	−0.030	5.072							NF sym str	1443.0	1444.7
0.927(11)	F$_4$	0.109	0.079	0.411	4.964						CN str	1398.0	1397.5
0.935(5)	F$_5$	−0.077	0.089	−0.063	−0.187	0.728					HCH bend	1167.0	1166.5
0.935(5)	F$_6$	0.114	−0.025	−0.103	−0.288	0.089	0.660				CH$_2$ wag	1047.0	1055.3
0.935(5)	F$_7$	0.041	−0.087	−0.142	0.223	0.171	0.063	0.957			NCH bend	857.5	848.0
0.976(21)	F$_8$	−0.038	0.031	0.512	0.015	−0.017	0.012	−0.035	1.863		FNF bend	558.0	558.6
0.976(21)	F$_9$	−0.119	0.049	0.647	0.524	−0.074	−0.113	−0.210	0.301	1.839	CNF sym bend	460.0	461.5

scale factors[b]		F$_{10}$	F$_{11}$	F$_{12}$	F$_{13}$	F$_{14}$	F$_{15}$	assignments	ω_{obs}	ω_{calcd}
0.887(5)	F$_{10}$	5.602						CH asym str	3027.0	3027.0
0.927(11)	F$_{11}$	0.032	3.698					NF asym str	1443.0	1447.1
0.935(5)	F$_{12}$	0.191	−0.107	0.674			A″	NCH asym bend	1134.5	1127.1
0.935(5)	F$_{13}$	−0.003	0.088	−0.117	0.661			NCH asym bend	836.0	835.6
0.976(21)	F$_{14}$	−0.110	0.642	−0.135	0.147	1.499		CNF asym bend	420.0	419.7
[1.0]	F$_{15}$	−0.010	0.034	−0.004	−0.002	−0.021	0.144	CN tors		282.9

[a] Stretches in aJ/Å^2, bends in aJ/rad^2, wavenumbers in cm^{-1}. Coordinates: see Table 2. [b] Identical values were refined in groups.

TABLE 4: Experimental and Theoretical Values for Structural Parameters of Difluoromethylamine[a]

	experimental		theoretical[b]			
	ED/MW[c]	MW[d]	HF	MP2	MP3	B3LYP
$\langle r(\mathrm{C-H})\rangle$[e]	1.104(4)	1.091(5)	1.079	1.084	1.084	1.088
$\Delta r(\mathrm{C-H})$[f]	[0.002]	0.002	0.002	0.002	0.002	0.002
$r(\mathrm{N-F})$	1.406(2)	1.413(5)	1.353	1.411	1.392	1.415
$r(\mathrm{C-N})$	1.467(6)	1.449(5)	1.448	1.458	1.460	1.462
$\angle\mathrm{C-N-F}$	104.1(2)	104.6(3)	105.8	103.7	104.2	104.3
$\angle\mathrm{F-N-F}$	101.7(2)	101.0(3)	102.4	101.9	101.9	101.8
$\angle\mathrm{N-C-H_1}$	109.9(11)	110.4(3)	110.7	110.8	110.7	111.3
$\angle\mathrm{N-C-H_6}$	106.5(10)	106.2(3)	107.1	106.6	106.8	106.6
$\angle\mathrm{H_6-C-H_7}$	110.6(28)	110.3(3)	110.0	110.2	110.1	110.0

[a] Distances (r) in angstroms, angles ($\angle_\alpha$) in degrees. Quantities in parentheses are estimated 2σ. [b] Distances are r_e. Basis set was 6-311++G(2d,2p). [c] This work. Distances are $r_\alpha 0$. [d] Ref 3. Distances are r_z. [e] $\langle r(\mathrm{C-H})\rangle = 0.5\cdot(r(\mathrm{C-H_1}) + r(\mathrm{C-H_6}))$. [f] $\Delta r(\mathrm{C-H}) = r(\mathrm{C-H_1}) - r(\mathrm{C-H_6})$.

TABLE 5: Distances and Vibrational Amplitudes in Methyldifluoroamine[a]

	$r_\alpha{}^0$	r_a	r_g	l_{exp}		l_{calcd}
C−H$_1$	1.104(5)	1.121	1.124	0.056	(5)	0.078
C−H$_6$	1.103(5)	1.121	1.123	0.056		0.078
N−F	1.406(2)	1.406	1.408	0.051	(3)	0.049
C−N	1.467(2)	1.467	1.469	0.052		0.050
N•H$_1$	2.115(12)	2.121	2.126	0.104		
N•H$_6$	2.071(12)	2.076	2.082	0.107		
C•F	2.265(4)	2.265	2.267	0.069	(4)	0.065
F•F	2.180(3)	2.179	2.181	0.067		0.063
F•H$_1$	2.451(16)	2.450	2.460	0.157		
F$_4$•H$_6$	2.530(20)	2.527	2.537	0.160		
F$_5$•H$_6$	3.217(8)	3.221	3.224	0.098		
H$_1$•H$_6$	1.825(12)	1.843	1.852	0.125		
H$_6$•H$_7$	1.813(35)	1.832	1.840	0.125		

[a] Values in angstroms. Quantities in parentheses are estimated 2σ. Amplitudes in brackets were refined as a group.

TABLE 6: Fits to Rotational Constants for Methyldifluoroamine[a]

isotope	A_0; B_0; C_0	A_z; B_z; C_z	ΔB_z [a]
CH_3NF_2	9857.186	9837.536	−2.700
	9653.337	9637.387	−2.665
	5463.855	5460.505	−2.721
$^{13}CH_3NF_2$	9650.286	9634.576	−2.291
	9502.218	9483.218	−0.747
	5353.879	5350.649	−2.054
CD_3NF_2	9096.309	9086.409	8.463
	8233.550	8220.210	2.197
	4924.541	4922.979	1.954
sym-CDH_2NF_2	9397.455	9384.855	1.563
	9288.763	9271.653	0.452
	5364.260	5361.030	−2.603
asym-CDH_2NF_2	9690.035	9674.215	−3.652
	9040.060	9024.770	4.458
	5218.680	5215.910	−0.147

[a] $\Delta B_z = B_z^{\mathrm{obs}} - B_z^{\mathrm{calc}}$.

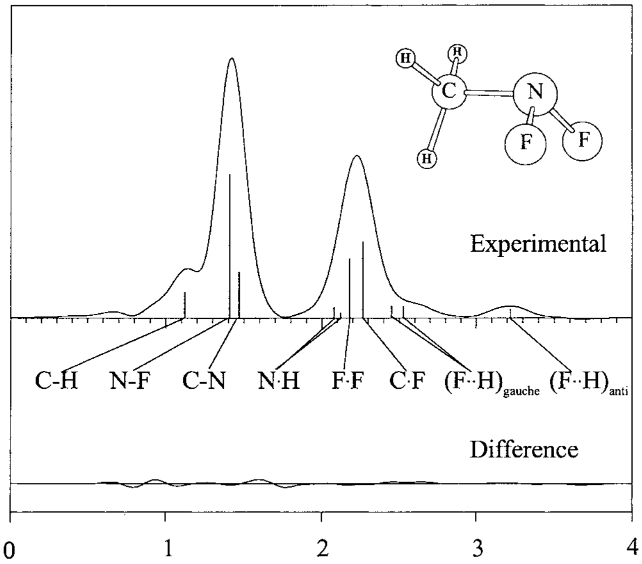

Figure 3. Radial distribution curves for methyldifluoroamine. The experimental curve is calculated from the average intensity curve with theoretical data for $s \leq 1.75$ Å^{-1} and with the convergence factor $B = 0.002$ Å^2. Vertical bars indicate interatomic distances, lengths of bars are proportional to the weights of the terms.

by modest scaling of a symmetrized force field based on Cartesian force constants obtained from theoretical calculations at the slightly higher MP2/6-311++G(d,f) level. We carried out similar force-constant calculations for the other molecules of the series, as well as calculations at other levels for comparison. For NF_3 and $MeNF_2$ with more than one N−F bond the value obtained for the symmetrized N−F stretching constant(s) from the theoretical Cartesian force field depends on the coordinates that describe them. If the full symmetries of these molecules are utilized in constructing the symmetry coordinates, both a symmetric and an asymmetric N−F stretching (symmetry) constant results and will have different values. If the symmetry restriction is dropped, only a single (valence) N−F stretching constant occurs. We have carried out both types of calculations with the results seen in Table 9. One notes that for the symmetric stretch Badger's rule is obeyed at all three levels of calculation: the value of the force constant increases with decreasing bond length. The same is true where symmetry restrictions are dropped—i.e., in a valence-force field—for the HF and B3LYP calculations, although for the latter the change between NF_3 and $MeNF_2$ is very small. It is only the valence-force field results at the MP2 level that display the contrary trend and hence might be considered a violation of the rule, but here also the magnitude of the changes is very small. We have also refined the MP2/6-311++G(d,p) force fields to fit the observed wavenumbers for the three $Me_nNF_{(3-n)}$ molecules. Excellent agreement was obtained, but in accord with general experience these "experimental" results differ slightly from the theoretical ones. The values from the symmetry force fields for NF_3, $MeNF_2$, and Me_2NF are, respectively, 6.00/3.38, 4.70/3.34, and 3.96 aJ/Å^2 for the symmetric/asymmetric N−F stretch; from a valence force field they are 4.00, 4.11, and 3.96 aJ/Å^2. The relationship between bond length and force constant value thus depends on the symmetry coordinates chosen for the comparison.

The molecules studied by Badger were both limited in number and small, and his force fields were very simple—hardly the symmetry fields we have employed. Further, in the cases of the polyatomic molecules (triatomic, five-atom tetrahedral, and

TABLE 7: Correlation Matrix (×100) for Parameters of Methyldifluoroamine

		s_{LS} [a] × 100	r_1	r_2	r_3	$\angle_4$	$\angle_5$	$\angle_6$	$\angle_7$	$\angle_8$	l_9	l_{10}	l_{11}
1	r(C−H)	0.16	100										
2	r(C−N)	0.20	−18	100									
3	r(N−F)	0.05	18	−79	100								
4	∠F−N−F	5.94	−51	−31	−71	100							
5	∠C−N−F	8.08	42	−71	55	−42	100						
6	∠N−C−H_1	37.7	−23	29	15	−6	10	100					
7	∠H_6−C−H_7	100.0	37	42	−14	−47	17	−3	100				
8	∠N−C−H_6	34.8	−33	−25	5	41	−30	−30	−69	100			
9	l(C−H)	0.51	−4	8	−5	1	−6	−2	4	−3	100		
10	l(C−N)	0.27	16	−80	69	−33	−60	24	−28	13	−33	100	
11	l(C·F)	0.40	−29	−27	5	37	−210	14	−62	58	37	−29	100

[a] σ_{LS} is the standard deviation from least squares.

TABLE 8: Structures of Some Fluoroamines from Microwave Spectroscopy and Electron Diffraction[a]

	H_2NF	HNF_2	NF_3		$MeNF_2$		Me_2NF
method:	MW[b]	MW[c]	MW[d]	MW[e]	ED/MW[f]	MW[g]	ED/MW[h]
$r(X-N)$	1.0225(3)	1.026(2)			1.467(6)	1.449(5)	1.462(7)
r(N−F)	1.4329(3)	1.400(2)	1.365(2)	1.371	1.406(2)	1.413(5)	1.447(6)
∠X−N−F	101.08(7)	99.8(2)			104.1(2)	104.6(3)	103.6(5)
∠F−N−F		102.9(2)	102.4(1)	102.2	101.7(2)	101.0(3)	

[a] Distances in angstroms, angles in degrees. Uncertainties in parentheses from different investigations have different meanings. [b] Ref 14. [c] Ref 15. [d] Ref 2b. [e] Ref 2a; uncertainties not given. [f] r_α^{o} values; this work. [g] Ref 3. [h] r_z values, ref 4.

TABLE 9: Calculated Values for N−F Stretch Force Constants/AJ·Å^{-2} in Fluoroamines

force field[a]	mode	NF_3	$MeNF_2$	Me_2NF
	HF/6-311++G(d,p)			
symmetry	sym str	9.17	7.50	5.89
	asym str	6.15	5.68	
valence		7.16	6.59	5.89
	MP2/6-311++G(d,p)			
symmetry	sym str	6.14	5.07	4.43
	asym str	3.51	3.70	
valence		4.38	4.39	4.43
	B3LYP/6-311++G(2d,2p)			
symmetry	sym str	5.84	4.78	3.86
	asym str	3.15	3.24	
valence		4.05	4.01	3.86

[a] The symmetry and valence force fields were obtained from the same Cartesian force fields.

seven-atom octahedral) it is not clear what wavenumbers or masses were used to derive the force constants. If one assumes the wavenumbers were from the symmetric stretches, then our results show that the rule applies *qualitatively* as well to NF_3, $MeNF_2$, and Me_2NF as it does to Badger's original examples. However, the rule defines a quantitative link between bond distances and bond stretching force constants, and it is clear from the range of force-constant values (Table 9) that the results will vary widely for the different sets. To the extent that there is any value at all in attempting to use Badger's rule in modern applications, it is worth noting that, scaled by the factor 0.927, the symmetry force constants for the symmetric N−F stretches obtained from MP2/6-311++G(d,p) calculations predict distances in excellent agreement with those observed: NF_3, 1.369 Å; $MeNF_2$, 1.414 Å; and Me_2NF, 1.448 Å.

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Supporting Information Available: Tables of the total scattered intensity from each plate, final backgrounds, molecular intensities from each plate, and averaged intensities from each camera distance (15 pages). See any current masthead page for ordering information and Web access instructions.

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