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The Microwave Spectra, Structure and Dipole Moment of "cis" N_2F_2 [*+]

Robert L. Kuczkowski and E. Bright Wilson, Jr.

Mallinckrodt Chemical Laboratories, Harvard University
Cambridge 38, Mass.

ABSTRACT

The microwave spectrum of one isomer of $F^{14}N^{14}NF$ and $F^{15}N^{14}NF$ is reported and from this the structure is derived as planar and "cis" with the following structural parameters: d(NN) = 1.214 ± 0.005A, d(NF) = 1.384 ± 0.01A, ∠FNN = 114 5° ± 0.5°. A dipole moment of 0.18±0.01D has been evaluated from the rotational Stark effect. Transitions of the molecule in an excited vibrational state are reported. From relative intensity measurements of this state, a vibrational frequency of 300 ± 35 cm^{-1} is estimated. A method is demonstrated enabling the ratio of nuclear spin statistical weights of two levels to be determined from the growth rate of their intensity with increasing Stark modulation voltage.

INTRODUCTION

Difluorodiazine (N_2F_2), which was first reported by Haller,[1] was recently separated into two isomeric species of different reactivity,[2,3,4] At the commencement of this study, the configuration of the less reactive species was accepted as being planar,

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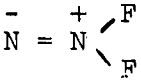
"trans" FNNF, while that of the more reactive species was uncertain as the following summary indicates:[5] 1) Prior to separation into two isomers, the electron diffraction pattern of N_2F_2 was interpreted as due to an equimolar mixture of "cis" and "trans" isomers with $d(N{=}N) = 1.25 \pm 0.04$ Å, $d(N{-}F) = 1.44 \pm 0.04$ Å and $\angle NNF = 115 \pm 5^\circ$. However the report notes that the configuration  $\overset{-}{N}=\overset{+}{N}F_2$ (called 1,1 difluorodiazine) could not be excluded on the basis of the diffraction pattern alone.[6] 2) The infrared spectra of the two separated isomers was interpreted in terms of the planar, "trans" FNNF structure for the less reactive species but considered as evidence against the "cis" FNNF structure for the more reactive species favoring the 1,1 difluorodiazine structure.[7] 3) Heats of formation of the two isomers were determined, showing the reactive species to be more stable by 3 Kcal.[8] 4) The similarity of mass spectral appearance potentials for the NF^+ and N_2F^+ fragments for both N_2F_2 isomers combined with the thermodynamic data above argued for a similarity in molecular structure, and hence "cis" and "trans" designations if other excitational energy effects are not involved in the dissociative ionization of either isomer.[9] 5) From assignment of the ^{19}F NMR spectra for both isomers and the qualitative features of the $^{19}F - \{^{14}N\}$ double resonance spectra, a "cis" structure was strongly favored over a 1-1 difluorodiazine structure for the more reactive species.[10]

Hence the situation presented to the microwave spectroscopist not merely the possibility of determining the molecular parameters but also of unambiguously deciding between the two proposed configurations.

EXPERIMENTAL

The samples of FNNF and $F^{15}NNF$ were obtained from Dr. Charles B. Colburn of Rohm and Haas Co., Redstone Arsenal Research Division, Huntsville, Alabama. They were prepared by Dr. Frederic A. Johnson and Dr. Charles O. Parker of those laboratories. The normal species sample was 85% "cis" isomer, 13% "trans" isomer. The spectra of the nitrogen 15 species was obtained from a sample prepared by enriching the starting materials to 31.65% in nitrogen 15. The purity of this sample was similar to the normal species sample except for some NF_3 which was not completely removed.

Conventional Stark modulated spectrometers were employed.[11] Frequencies were measured by a conventional frequency standard and also with a Gertsch FM4A locked to a Gertsch FM6 frequency meter; both standards were checked with a standard 100 kc signal from the Cruft Laboratory of Harvard University. Measurements were reproducible to 0.1 Mc and were obtained at dry ice temperature. Relative intensities were determined by a technique developed in these laboratories.[12]

SPECTRUM

The spectra observed were characteristically sparse, weak in intensity and had incompletely modulated Stark transitions. Only b-type transitions were identified. The observed and calculated spectra for the two isotopic species are listed in Table I. The calculated spectra used values of A, B, and C given in Table II. These rotational constants were determined from the $0_{00} \rightarrow 1_{11}$, $1_{01} \rightarrow 1_{10}$, $2_{02} \rightarrow 2_{11}$ transitions. Deviations for the calculated and observed transitions for the higher J states are attributed to centrifugal distortion. Because of the small dipole moment, the Stark effect could not be employed to identify transitions. However, the sparseness of the spectrum enabled a frequency fit to be easily realized. The intensities of the isotopic species were consistent with the known purity and isotopic enrichment of the sample. Moreover, the small change in inertial defect for the normal and isotopic species further confirms the assignment. The assignment to the excited vibrational state was confirmed by the large change in inertial defect and the temperature dependence of the intensity of these lines relative to the ground state lines.

EXCITED VIBRATIONAL STATE

Measurement of the ratio of the intensities of the ground state and excited vibrational state transitions was accomplished by comparing peak signals at the same Stark voltage with the assumption that in this manner effects from incomplete Stark modulation would cancel out. The intensity ratios obtained are listed in Table III. The relatively large uncertainty in the measurements is due to the low intensity of the observed lines. In order to calculate the vibrational frequency (once the structure is determined as "cis"), one uses the Boltzmann distribution formula and needs to know the temperature and the nuclear spin statistical weight of the levels involved since a rotation about the b axis exchanges equivalent nitrogen and fluorine atoms. Two possibilities exist for the nuclear spin statistical weight: a) If the excited vibrational state observed is symmetric to the rotational symmetry axis, then the statistical weight will be the same as in the ground state. b) If the excited vibrational state is antisymmetric then the ratio of weights (excited state over ground state) will be 7/5 if the parity of $K_{-1} \times K_{+1}$ is even, and 5/7 otherwise.

The intensity ratios observed indicate that the nuclear spin ratio is unity and hence a mode of vibration symmetric to the two-fold axis is involved with a vibrational frequency of 300 ± 35 cm^{-1}. Two sufficiently low frequency modes of vibration could qualify: the torstional mode, or the symmetrical N-F bending mode. Comparison with other molecules suggests that the symmetrical N-F bending mode should be the lowest frequency for the molecule. Further evidence for this is provided by a rough argument about the contribution of these modes to the inertial defect. If one assumes that the torsional mode has the lowest frequency and is therefore responsible for the observed satellite, and further makes an assignment of the other frequencies, it is possible to put limits on the Coriolis constants and demonstrate that the inertial defect should be more negative for the satellite than for the ground state.[20,21] This is contrary to observation. On the other hand similar rough arguments do come out with the correct sign if the lowest frequency is the N-F bending. Because the nuclear spin ratio of 7/5 or 5/7 is close to unity and because of the large estimated error in the intensity ratios, an antisymmetric vibration cannot be completely excluded, but this possibility is not considered likely since the intensity ratios then yield a decidedly poorer degree of consistency.

If the vibration frequency obtained here is correctly assigned to the symmetric N-F bend then the vibrational analysis[7] which favored the $N{=}NF_2$ structure cannot be valid and hence does not provide any support for this structure.

DIPOLE MOMENT

The dipole moment was determined from the $2_{02} \rightarrow 2_{11}$ transition from the variation in the displacement of the M=2 component as a function of voltage. The Stark effect of the $1 \rightarrow 2$ transition of OCS, using a dipole moment of 0.7124 D, was employed to calibrate the spectrometer. A least squares fit of the data gave a Stark coefficient of $2.7 \pm 0.3 \times 10^{-7}$ Mc/(V^2/cm^2). The dipole moment was calculated to be 0.18 ± 0.01 D.

In calculating the dipole moment, the effect of the nitrogen nuclear quadrupole moment did not have to be accounted for since nothing definitely attributable to it was observed. Inspection of the theory shows that the $0_{00} \rightarrow 1_{11}$ transition depends only on the parameter $\chi_{aa}(1 + \eta)$.[13] No observable splitting was detected for this transition from which it is estimated that $\chi_{aa}(1 + \eta) < 2$ Mc.

The small value of the dipole moment is similar to the value 0.24 D for NF_3[14] and 0.27 D for N_2F_2[15] and is usually attributed to the hybridized lone pair of the nitrogen atom counteracting the N-F bond moment.

STRUCTURE

Two points can be noted from the values of the moments of inertia for the two isotopic species. First, the small, positive value of the inertial defect for both species attests to the planarity of the molecule. Second, the large change in I_B upon isotopic substitution is incompatible with the 1-1 structure $N{=}NF_2$, since in this molecule both nitrogens would lie on the "b" axis and hence, in the rigid rotor limit, no change should occur for different isotopic species. The only possible symmetric structure remaining is the "cis" model.

The "a" and "b" coordinates are listed in Table IV. See Figure 1 for definition of the coordinate system. The nitrogen coordinates were determined from Kraitchman's equations.[16] The fluorine "b" coordinate was determined from the relation $\sum_i m_i b_i = 0$. The fluorine "a" coordinate was determined from $I_b = \sum_i m_i a_i^2$. Structural parameters derived from these coordinates are also listed in Table III.

The structure calculated in the above manner is not exactly the equilibrium structure because of the zero point vibrations. However, we believe by comparison with other molecules that the so-called "average" structure[20,21] very likely is included within the limits $d_{NN} = 1.214 \pm 0.005$ Å, $d_{NF} = 1.384 \pm 0.01$ Å, and $\angle NNF = 114.5^{\circ} \pm 0.5^{\circ}$.

Even before the isotopic sample was received, it was nevertheless possible to support the cis structure, on the basis of the 7 to 5 alternating intensities expected, in contrast with the 3 to 1 ratios predicted for the planar 1-1 form. However, the determination of the experimental intensity ratios for pairs of different rotational transitions was not quite straightforward because the Stark voltage available was not sufficient for complete modulation. The technique used is described in the Appendix.

The moments of inertia for the normal isotopic form alone were not sufficient to distinguish between the two forms, being compatible with either if suitable bond lengths and angles are used. However, the required angles made the 1-1 form somewhat less likely.

DISCUSSION

The structure can be rationalized as being similar to the isoelectronic "cis" 1,2 difluoroethylene HFC=CFH. There are not many NN double bonds uncomplicated by resonance structures to use for comparison. In $CH_3N{=}NCH_3$ (K) d(NN) = 1.24 ±0.05; in ϕ - N=N - ϕ d(NN) = 1.25 ±0.04 (M); in cyclic diazirine, CH_2N_2, d(NN) = 1.228 ± 0.003 A°.[22] This scant data suggests that a shortening of the d(NN) distance of a few hundredths of an Angstrom may be occurring. This would be consistent with evidence accumulating in support of the shortening of multiple bonds by fluorine substitution, illustrated for example in the fluoroethylenes or COF_2.[23,24] The d(NN) shortening is to be contrasted with the pronounced d(OO) shortening and d(FO) lengthening observed in FOOF.[25] If the effect in F_2O_2 could be explained in terms of ionic contributions F^-O^+-O-F arising from the electronegativity difference between F and O, one might expect a similar marked shortening in N_2F_2. The absence of this weighs against the ionic explanation for F_2O_2.

The d(N-F) of 1.385 ± 0.01 Å in FNNF can be compared with 1.400 ± 0.002 A in NF_2H,[26] 1.35 Å in FNO_2,[27] 1.371 in NF_3, and 1.52 in FNO.(b) The long d(NF) in FNO has been explained in terms of large contributions due to $F^-\ N^+O$ structures.[28,29] This does not explain why such structures contribute in FNO but not in other molecules such as FNNF. It appears possible that the same effect may be occurring in F_2O_2 and FNO (also ClNO and BrNO) because the alternative explanation proposed for the qualitative features of F_2O_2 based on the molecular orbital representation[25] can also be applied to FNO. This approach accounts adequately for the qualitative bond lengths in these molecules but also explains the absence of the phenomenon in a molecule like FNNF as a diagram of the molecular orbitals in N_2 will clearly indicate. It is interesting to note that the structure of NSF recently determined in these laboratories as d_{NS} = 1.446 Å, d_{SF} = 1.646$^{\circ(1)}$ exhibits a long SF distance and a short SN distance and,considering the valence shell electrons in the sulfur and nitrogen,is electronically similar to NO. However, an alternative explanation is possible here for the short d(SN) in terms of a triple sulfur nitrogen bond.

The value 114°28' for the N=N-F angle is within the range reported for other X=N-Y molecules, some of which are listed in Table IV. The decrease below 120° is usually rationalized by stating that unshared pairs are more diffuse than bonding elections[17,18] an idea supported by other examples.

Notable exceptions to this view are found in cyanic acid (HNCO) and its derivatives HNCS and CH_3NCS. However, as noted by Beard and Dailey,[19] the value of the angle C-NC in CH_3-N-CS and the short N-C distance (1.22A) signify an important contribution from the $H_3C\text{-}N^+\equiv C\text{-}S^-$ resonance structure. In HNCO and HNCS the C=N bond is 1.207 A and 1.216 A respectively and is similarly short. (The C=N bond in formaldoxime (H_2C=N-OH) is 1.276 A. The C N distance in hydrogen cyanide (HC≡N) is 1.15 A).

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APPENDIX

Intensity Ratios for Partially Modulated Lines

When insufficient Stark voltage can be applied to resolve all the Stark lobes completely from the main line, the peak height observed in a Stark effect microwave spectrometer depends on the dipole moment, the electric field, the Stark coefficients for the transition and the line width, as well as on the true line intensity. With the assumption of a Lorentz shape for the line and for each Stark component (the latter with opposite sign as displayed with a phase-sensitive detector), and with the normal form

$$\Delta \nu = (A + BM^2)\,\mu^2 \mathcal{E}^2$$

for the ordinary second-order Stark shifts, it is straightforward to expand the expression for the maximum height of the line as a power series in the square of applied field $\mathcal{E}$. For a Q branch transition, the limiting expression for the peak height vs $\mathcal{E}^2$ is then given by

$$\frac{3}{8}\sqrt{3}\, I_o \left\{A + \frac{1}{5}[(6J^3 + 9J^2 + J-1)/(2J + 1)]\, B\right\} (\mu^2 \mathcal{E}^2/b)$$

in which I_o is the peak intensity with full modulation and b is the half width at half height of the line.

By obtaining the ratio of the initial slopes for two lines of known J, A, and B, the ratio of their I_o's can be obtained. This then extends the technique of relative intensity measurements with a Stark effect spectrometer to cases of incomplete modulation.

Table I. Assigned rotational transitions(Mc)

Transition	Obs. Freq.	Cal. Freq.
	$F^{14}N\ ^{14}NF$(ground vib. state)	
$1_{01} \rightarrow 1_{10}$	14035.46	14035.46
$2_{02} \rightarrow 2_{11}$	16635.65	16635.65
$3_{03} \rightarrow 3_{12}$	21058.50	21059.00
$0_{00} \rightarrow 1_{11}$	25338.23	25338.22
$4_{04} \rightarrow 4_{13}$	27727.67	27729.21
$5_{14} \rightarrow 5_{23}$	32232.12	32232.31
$3_{12} \rightarrow 3_{21}$	33471.32	33472.01
$6_{15} \rightarrow 6_{24}$	34482.72	34485.30
$2_{11} \rightarrow 2_{20}$	35524.22	35525.05
$1_{01} \rightarrow 2_{12}$	36641.03	36640.98
$5_{05} \rightarrow 5_{14}$	36795.75	36799.61
$7_{16} \rightarrow 7_{25}$	39307.47	39314.02
	$F^{15}N\ ^{14}NF$(ground vib. state)	
$1_{01} \rightarrow 1_{10}$	13706.43	13706.43
$2_{02} \rightarrow 2_{11}$	16326.55	16326.55
$3_{03} \rightarrow 3_{12}$	20794.40	20795.32
$0_{00} \rightarrow 1_{11}$	24899.32	24899.31
$1_{01} \rightarrow 2_{12}$	36092.10	36092.19
	$F^{14}N\ ^{14}NF$(excited vib. state)	
$1_{01} \rightarrow 1_{10}$	14180.73	14180.73
$2_{02} \rightarrow 2_{11}$	16747.3 ± 0.5	16747.35
$3_{03} \rightarrow 3_{12}$	21103.3 ± 0.5	21105.24
$7_{16} \rightarrow 7_{25}$	39287.64	39295.96
$0_{00} \rightarrow 1_{11}$	25418.70	25418.69
$1_{01} \rightarrow 2_{12}$	36656.50	36656.65

Table II. Rotational constants(Mc)and moments of inertia(amuA^2)*

	$F^{14}N\ ^{14}NF$(gd)	$F^{15}N\ ^{14}NF$(gd)	$F^{14}N\ ^{14}NF$(exc.vib.)
A	19686.84	19302.87	19799.71
B	7946.76	7901.20	7890.59
C	5651.38	5596.44	5618.98
I_A	25.6786	26.1894	25.5322
I_B	63.6147	63.9815	64.0675
I_C	89.4525	90.3308	89.9684
ΔI	0.1592	0.1599	0.3687

* Conversion factor 5.0553×10^5 Amu A^{2}Mc.

Table III. Relative intensities, FNNF, excited vib. state/ground state

Transition	Temperature	Ratio of Intensities	ν(sym.vib.)	ν(anti.vib.)
$0_{00} \rightarrow 1_{11}$	299°K*	0.22 ± 0.06	314 cm^{-1}	384 cm^{-1}
$2_{02} \rightarrow 2_{11}$	195°K+	0.10 ± 0.05	312	358
$3_{03} \rightarrow 3_{12}$	195°	0.12 ± 0.05	287	241
$1_{01} \rightarrow 2_{12}$	195°	0.11 ± 0.05	298	253

* Room temperature on day of measurement

\+ Dry ice packed around waveguide and hence dry ice temperature assumed.

Table IV. Coordinates (A) of atoms in principal axis system of FNNF and structure*

	Nitrogen	Fluorine
$\lvert a \rvert$	0.607	1.184
$\lvert b \rvert$	0.725	0.534
d(NN)	1.214	
d(NF)	1.384	
FNN	$114^{\circ}28'$	

*Masses from Townes and Schawlow "Microwave Spectroscopy", McGraw-Hill Book Co., Inc. New York, 1955.

Table V. Comparison of X-N=Y angles

Molecule		Angle	Reference
"cis" F-N=N-F		$114.5 \pm 0.5^\circ$	this work
H-N=O		108.6°	a
F-N=O		110°	b
Cl-N=O		$114 \pm 3^\circ$	c
Br-N=O		114°	d
H_2C=N-OH		112.2°	e
$(CH_3)_2C$=N-OH		110°	f
H-N=NN		$112.7 \pm 0.5^\circ$	g
HO-N=O	"cis"	$114 \pm 2^\circ$	h
	"trans"	$118 \pm 2^\circ$	h
NO_2^-		$115.7 \pm 3^\circ$	i
H-N=SO "cis"		$117.2 \pm 0.4^\circ$	j
CH_3-N=N-CH_3	"trans"	$110 \pm 10^\circ$	k
CH_3-N=NN		$120 \pm 5^\circ$	l
ϕ-N=N-ϕ	"cis"	$125^\circ \pm 4^\circ$	m
	"trans"	$121^\circ \pm 4^\circ$	m
H-N=CO		$128.1 \pm 0.5^\circ$	n
H-N=CS		$130.2 \pm 0.2^\circ$	o
H_3C-N=CS		142°	p

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Figure 1. Structure and Coordinates of cis N_2F_2.