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Microwave Spectrum, Structure, Dipole Moment, Quadrupole Coupling Constant, and Internal Motion of Thioformamide

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The r_s structure of thioformamide has been determined from the microwave spectra of the normal as well as isotopic species of the molecule. The structural parameters obtained assuming the planarity of the molecule are $N\text{–}H_c = 1.001_8 \pm 0.006$ Å, $N\text{–}H_t = 1.006_5 \pm 0.003$ Å, $C\text{–}N = 1.358_2 \pm 0.003$ Å, $C\text{–}S = 1.626_2 \pm 0.002$ Å, $C\text{–}H_a = 1.09_6 \pm 0.08$ Å, $\sphericalangle H_cNH_t = 121°42' \pm 40'$, $\sphericalangle H_cNC = 117°55' \pm 40'$, $\sphericalangle H_tNC = 120°22' \pm 30'$, $\sphericalangle NCS = 125°16' \pm 15'$, $\sphericalangle NCH_a = 108°_{5'} \pm 5°$, and $\sphericalangle SCH_a = 126°_{39'} \pm 5°$.

The dipole moment is calculated from the Stark effects of the three transitions to be $\mu_a = 3.99 \pm 0.02$ D, $\mu_b = 0.13 \pm 0.25$ D, and $\mu_{\text{total}} = 4.01 \pm 0.03$ D, where the *c* component is assumed to be zero.

The quadrupole coupling constant of the ^{14}N nucleus is estimated using the doublet splittings observed for six *Q*-branch transitions; $\chi_{cc} - \chi_{bb} = -5.39 \pm 0.15$ MHz and $\chi_{aa} = 2.9 \pm 1.2$ MHz.

Two sets of vibrational satellites are observed and assigned to the first excited state of the amino wagging and the NCS bending vibrations, respectively. The relative intensity measurement gives the vibrational energies of 393±40 cm^{-1} and 457 ± 50 cm^{-1} for NH_2CHS and 293 ± 30 cm^{-1} and 393 ± 40 cm^{-1} for ND_2CHS. The amino wagging inversion vibration in the molecule is discussed in comparison with that in formamide. It is most probable that the thioformamide molecule is also planar without any potential hump to the amino inversion at the planar configuration.

INTRODUCTION

Because of interest in the labile structure of the amino or imino group, many spectroscopic investigations have been carried out extensively on a number of amides (*1–11*). The amino group in simple amides takes normally a nonplanar configuration at the equilibrium, and thus executes an inversion-type motion with double-minimum potential function. The barrier height is in most cases low enough to split each energy levels of the inversion. Formamide might be an exceptional case of nearly zero potential barrier to the amino inversion (*10–12*). The low barrier is ascribed to the resonance form (*b*) of Fig. 1. In fact, the N–C distance reported by Costain and Dowling (*11*) is 1.376 ± 0.010 Å, much smaller than that in methyl amine, 1.4714 Å (*2*). It might then be interesting to investigate molecules related closely to formamide and to compare the barrier height with that in formamide. The microwave spectrum of carbamyl fluoride H_2NCFO has already been reported (*13*), but no detailed information was obtained on the amino inversion. In the present work thioformamide H_2NCHS is investigated by microwave spectroscopy. Because the sulfur atom is less electronegative than the oxygen

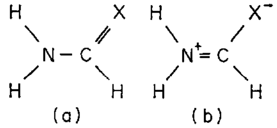

FIG. 1. Resonance forms of formamide ($X = O$) and thioformamide ($X = S$).

atom, it might be expected that the resonance form (*b*) of Fig. 1 contributes less in thioformamide than in formamide. If this is the case, the amino group will be bent out of the molecular plane to a larger extent and the N–C bond will be longer.

Recently Brittain *et al.* (*14*) reported the microwave spectrum of aminodifluorophosphine H_2NPF_2 and concluded that the PNH_2 group was in a plane bisecting the FPF angle, and they explained the planar configuration in terms of the p_π–d_π bonding character of the N–P bond. The N–P length was actually shorter than that normally reported. A similar result was obtained for dimethylaminodifluorophosphine, $PF_2N(CH_3)_2$ (*15*). Lovas and Johnson (*16*) also concluded a planar structure of the C_{2v} symmetry for aminodifluoroborane BF_2NH_2 from the microwave spectrum, and the B–N bond was presumed to have double-bond character.

EXPERIMENTAL DETAILS

The normal species of thioformamide was synthesized by the method of Gabriel (*17*): phosphorus pentasulfide was added to formamide at 0°C and stirred for 24 hr, and the raw product of thioformamide was then purified according to the procedure of Willstätter and Wirth (*18*). The deuterated species, ND_2CHS and NHDCHS, were prepared by the exchange reaction with heavy water.

The spectrometer used was of conventional Hughes–Wilson type with a 110 or 120 kHz oscillator as a Stark modulator. The spectra were recorded at room temperature, while the sample was pumped continuously through the cell.

ROTATIONAL SPECTRA

Both the *a*-type and *b*-type transitions are observed and assigned for the normal, deuterated, and ^{34}S species, whereas only the *a*-type *R*-branches are detected for the ^{15}N and ^{13}C species, because the *b*-component of dipole moment is much smaller than the *a*-component. The spectra of the latter two species are observed in natural abundance. Assignment is confirmed by heating the cell up to about 100°C to eliminate possibilities of the lines being due to the excited vibrational states. Absence of the hyperfine structure due to the nitrogen quadrupole coupling is an additional evidence for the assignment of the ^{15}N spectra. Observed frequencies are listed in Table I. The rotational constants are determined using appropriate low-J transition frequencies, as shown in Table II, where the effect of centrifugal distortion is neglected. Differences between the observed and calculated frequencies are also given in Table I.

The inertia defects listed in Table II are all positive, but show variations with isotopic substitution similar to those observed by Costain and Dowling for formamide (*11*). In particular, a deuterium substitution at the amino hydrogen trans to the $C = S$ bond (hereafter referred to as H_t) decreases the inertia defect by about 0.022 amu Å^2, which may be compared with 0.024 amu Å^2 for formamide.

MOLECULAR STRUCTURE

As a first approximation the molecule is assumed to be planar. This assumption is primarily based upon the fact that the inertia defect is positive for all isotopic species studied. Even if the out-of-plane coordinates of atoms are not zero, it is difficult to determine them directly from Kraitchman's equation. As will be discussed below, thioformamide is probably planar in view of the results on formamide (*12*).

The A constant has not been determined for the ^{15}N and ^{13}C species. The inertia defect is estimated by analyzing the normal coordinates. In Table II the calculated inertia defect, and also the I_a moment and the A constant, which are obtained using the calculated inertia defect, are given in parentheses for the ^{15}N and ^{13}C species.

Kraitchman's equation for a planar molecule is used to calculate the a and b coordinates of atoms of Table III except for the aldehyde hydrogen H_a, for which an approp-

TABLE I. Rotational Transitions of Thioformamide in the Ground Vibrational State (MHz)

Species	normal		cis-D[a]		trans-D[a]		D_2	
transition	obs	o-c	obs	o-c	obs	o-c	obs	o-c
$1_{01}\leftarrow0_{00}$	11 651.70	0.00	11 261.87	-0.01	10 865.12	0.00	10 537.61	-0.01
$2_{12}\leftarrow1_{11}$	22 751.62	0.00	21 914.00	-0.02	21 249.68	0.00	20 539.40	-0.02
$2_{02}\leftarrow1_{01}$	23 298.58	-0.74	22 517.26	-0.51	21 726.86	-0.29	21 070.74	0.12
$2_{11}\leftarrow1_{10}$	23 855.44	0.26	23 132.76	-0.74	22 210.92	0.12	21 612.42	1.36
$3_{13}\leftarrow2_{12}$	34 124.40	-0.49	32 867.15	-0.15	31 871.20	-1.40	30 805.88	-0.37
$3_{12}\leftarrow2_{11}$	35 780.16	-0.05	34 695.04	-1.45	33 314.68	0.42	32 415.04	1.35
$1_{11}\leftarrow0_{00}$	67 303.27	-0.49	57 504.88	0.29	66 698.28	0.00		
$1_{10}\leftarrow1_{01}$	56 203.84	0.00	46 852.45	0.00			46 826.55	0.00
$2_{11}\leftarrow2_{02}$	56 759.95	0.25	47 467.97	-0.21			47 367.68	0.69
$3_{12}\leftarrow3_{03}$	57 601.70	0.56	48 402.20	-0.78	57 531.25	2.62	48 188.02	1.70
$4_{13}\leftarrow4_{04}$					58 518.32	3.91		
$5_{14}\leftarrow5_{05}$					59 769.25	5.34		

Species	^{34}S			^{13}C		^{15}N	
transition	obs	o-c	transition	obs	o-c	obs	o-c
$1_{01}\leftarrow0_{00}$	11 377.36	0.00	$3_{13}-2_{12}$	33 971.28	0.31	33 156.68	0.14
$2_{12}\leftarrow1_{11}$	22 227.60	0.00	$3_{12}-2_{11}$	35 662.16	-0.01	34 729.05	-0.02
$2_{02}\leftarrow1_{01}$	22 747.20	-3.79	$4_{14}-3_{13}$	45 289.53	-0.02	44 204.45	0.01
$2_{11}\leftarrow1_{10}$	23 281.96	0.12	$4_{13}-3_{12}$	47 544.25	0.13	46 301.49	0.43
$4_{13}\leftarrow4_{04}$	58 624.98	1.41					
$5_{14}\leftarrow5_{05}$	60 001.59	2.25					
$6_{15}\leftarrow6_{06}$	61 683.46	2.85					

a. cis-D denotes a species that contains amino deuterium cis to C=S and trans-D trans to C=S.

TABLE II. Rotational Constants (MHz), Moments of Inertia (amu Å^2), and Inertia Defects (amu Å^2) of Thioformamide in the Ground Vibrational State[a]

Species	normal	^{15}N	^{13}C	^{34}S	cis-D[b]	trans-D[b]	D$_2$
A	61 753.80	(61 297.$_1$)[c]	(59 980.$_3$)[c]	61 630.62	52 178.52	61 506.00	51 827.45
B	6 101.74	5 919.61	6 085.09	5 952.24	5 935.81	5 672.84	5 536.72
C	5 549.96	5 395.43	5 521.35	5 425.12	5 326.07	5 192.28	5 000.90
I_a	8.183 72$_3$	(8.244$_7$)[c]	(8.425$_7$)[c]	8.200 08$_0$	9.685 51$_8$	8.216 69$_4$	9.751 12$_6$
I_b	82.824$_9$	85.373$_2$	83.051$_5$	84.905$_2$	85.140$_2$	89.086$_9$	91.277$_1$
I_c	91.059$_4$	93.667$_4$	91.531$_2$	93.154$_8$	94.887$_2$	97.332$_2$	101.057$_0$
Δ	+0.050$_8$	(+0.049$_5$)[c]	(+0.054$_0$)[c]	+0.049$_5$	+0.061$_5$	+0.028$_6$	+0.028$_8$

a. Conversion factor is 505376 MHz amu Å^2.

b. See footnote a of TABLE I.

c. Calculated using estimated inertia defects, see text.

riate isotopic species is not available. The first-moment equations, $\sum_i m_i a_i = 0$ and $\sum_i m_i b_i = 0$, lead to $a(\mathrm{H}_a) = -0.802$ Å and $b(\mathrm{H}_a) = -1.639$ Å for H$_a$. However, these numbers are not compatible with the cross-product condition, $\sum_i m_i a_i b_i = 0$, as shown in Fig. 2. A point in Fig. 2, $a(\mathrm{H}_a) = -0.78 \pm 0.04$ Å and $b(\mathrm{H}_a) = -1.59 \pm 0.06$ Å, might be a better estimate of the position of H$_a$; the three conditions become

TABLE III. The r_s Coodinates of Atoms in Thioformamide (Å)

Atom	a_s	b_s
N	-1.611$_1$	+0.25$_4$
C	-0.478$_3$	-0.495$_9$
S	+1.037$_4$	+0.093$_3$
H$_c$[a]	-1.513$_9$	+1.250$_6$
H$_t$[b]	-2.514$_5$	-0.190$_0$
H$_a$[c]	-0.78	-1.55

a. H$_c$ denotes an amino hydrogen cis to the C=S bond.

b. H$_t$ denotes an amino hydrogen trans to the C=S bond.

c. H$_a$ denotes the aldehyde hydrogen.

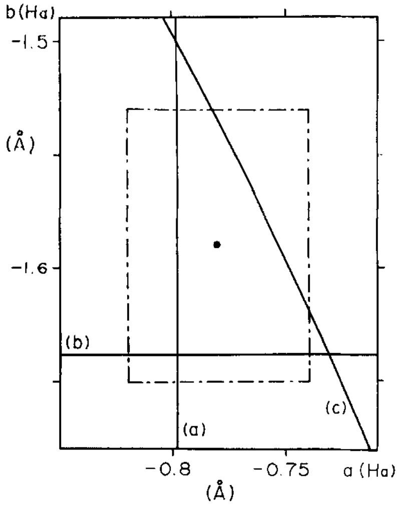

FIG. 2. a versus b coordinates of H_a. Curves (a), (b), and (c) denote $\Sigma_i m_i a_i = 0$, $\Sigma_i m_i b_i = 0$, and $\Sigma_i m_i a_i b_i = 0$. A closed circle indicates the final values of the coordinates with estimated error limits designated by broken lines.

$\sum_i m_i a_i = +0.022$ amu Å, $\sum_i m_i b_i = +0.049$ amu Å, and $\sum_i m_i a_i b_i = -0.043$ amu Å^2. They also give rise to a reasonable value for $\sum_i m_i a_i^2 = 82.795$ amu Å^2 compared with the observed value 82.824_9 amu Å^2, but lead to the b-moment $\sum_i m_i b_i^2$ of 8.290 amu Å^2, somewhat larger than the observed 8.18372_3 amu Å^2. The $b(H_a)$ coordinate is thus slightly adjusted to -1.55 ± 0.07 Å.

The distance between the two amino hydrogens may also be calculated by choosing the D_2 species, D_2NCHO, as a parent molecule. It is calculated to be 1.748 Å, which is to be compared with 1.754 Å in the normal species.

The b coordinate of the sulfur atom might be considered inaccurate, but, because the mass change here is two atomic mass units and the I_a moment is determined much more accurately than the I_b moment, the $b(S)$ coordinate derived should be accurate to ± 0.003 Å. Other coordinates are large enough to calculate the structural parameters, which are listed in Table IV, where the errors are estimated to encompass uncertainties due to the zero-point vibrations.

DIPOLE MOMENT

Stark effects of three transitions are measured quantitatively as shown in Table V, using the OCS molecule as a standard (*19*). In analyzing the observed Stark coefficients the c component of dipole moment is assumed to be zero.

Although the Stark effects of the $3_{12} \leftarrow 3_{03}$ transition is as sensitive to the b component of dipole moment as to the a component, the b component is determined much less accurately, because it is much smaller than the a component.

NITROGEN QUADRUPOLE COUPLING CONSTANT

A few transitions of the species except for the ^{15}N species are split due to the nitrogen quadrupole coupling. In particular some of the Q-branch transitions are observed as

TABLE IV. Molecular Structure of Thioformamide[a]

$N{-}H_c$	$1.001_8 \pm 0.006$ Å
$N{-}H_t$	$1.006_5 \pm 0.003$ Å
C-N	$1.358_2 \pm 0.003$ Å
C-S	$1.626_2 \pm 0.002$ Å
$C{-}H_a$	$1.09_6 \pm 0.08$ Å
$\angle H_cNH_t$	121°42′ ± 40′
$\angle H_cNC$	117°55′ ± 40′
$\angle H_tNC$	120°22′ ± 30′
∠NCS	125°16′ ± 15′
$\angle NCH_a$	$108^\circ{}_{5'} \pm 5^\circ$
$\angle SCH_a$	$126^\circ{}_{39'} \pm 5^\circ$

a. See footnotes of TABLE III for H_c, H_t, and H_a.

doublets; those of the normal species are listed in Table VI. In these transitions the $F' = J + 1 \leftarrow F = J + 1$ and $F' = J - 1 \leftarrow F = J - 1$ are not resolved. When splittings are interpreted as those between the $F = J + 1$ and $F = J$ components, the standard technique of analysis gives set I of Table VI, whereas set II is obtained taking the unresolved lines as the average intensity of the two unresolved components. Set I gives slightly better agreement of the calculated splittings with the observed than

TABLE V. Stark Effect and Dipole Moment of Thioformamide

Transition	$\|M\|$	Stark coefficient (10^{-5}MHz/(volt/cm)^2) obs	obs - calc
$1_{01} \leftarrow 0_{00}$	0	18.47_3	0.002
$2_{02} \leftarrow 1_{01}$	1	4.411	0.123
	0	-5.397	-0.119
$3_{12} \leftarrow 3_{03}$	3	7.716	0.013
	2	3.389	0.078

$\mu_a = 3.99 \pm 0.02$ D

$\mu_b = 0.13 \pm 0.25$ D $\qquad \mu_{total} = 4.01 \pm 0.03$ D

$\mu_c = 0$ (assumed)

TABLE VI. Nitrogen Quadrupole Hyperfine Structure and Coupling Constant of Thioformamide (MHz)[a]

Transition	Splitting		
	obs.	obs-calc I	obs-calc II
$6_{15} \leftarrow 6_{16}$	1.89 ± 0.02	-0.004	+0.015
$7_{16} \leftarrow 7_{17}$	1.85 ± 0.06	+0.051	+0.055
$8_{17} \leftarrow 8_{18}$	1.93 ± 0.03	-0.018	-0.026
$5_{14} \leftarrow 5_{05}$	1.08 ± 0.03	+0.006	+0.014
$6_{15} \leftarrow 6_{06}$	1.10 ± 0.03	-0.011	-0.010
$7_{16} \leftarrow 7_{07}$	1.11 ± 0.02	-0.007	-0.012

	I	II
$\chi_{cc} - \chi_{bb}$	-5.39 ± 0.15	-5.09 ± 0.12
χ_{aa}	2.9 ± 1.2	2.4 ± 0.8
χ_{bb}	1.2 ± 0.6	1.4 ± 0.4
χ_{cc}	-4.2 ± 0.6	-3.7 ± 0.4

a. See the text for calc I and calc II.

set II, although the differences between the two sets are within estimated errors. It is seen that $\chi_{cc} - \chi_{bb}$ is determined fairly accurately while χ_{aa} is not.

VIBRATIONAL SATELLITES

So far as the ground-state spectrum is concerned, no anomaly is observed which may be due to intramolecular motions of large amplitudes. Search is therefore made for vibrational satellites to obtain more detailed information on the intramolecular motions. Two sets of strong satellites were observed, not only for the normal species, but also for the three deuterated species, as shown in Table VII. The two vibrations giving rise to these satellites are hereafter referred to as ν_{I} and ν_{II}.

Relative intensity measurements reveal that isotopic shift of vibrational frequency on deuteration is much larger for ν_{I} (293/393 = 0.746) than for ν_{II}(393/457 = 0.860). Furthermore, the ν_{II} satellite is accompanied by another set which may be due to the overtone state, because the latter appears at a frequency twice as far away from the ground-state line as the ν_{II} spectrum. The ν_{II} satellite is therefore assigned to the NCS bending vibration. Vibrational frequencies obtained from relative intensity, 457 ± 50 and 393 ± 40 cm^{-1} for the normal and the dideuterated species, may be compared favorably with the infrared values, 439 and 400 cm^{-1} (*20*).

On the other hand, no satellite that may be ascribed to the overtone state is observed for the ν_I vibration. The ratio of vibrational frequencies of the two isotopic species, 0.746, is close to the square root of the mass ratio m_H/m_D, 0.707. It is therefore probable that the ν_I vibration is mainly associated with the amino group, probably with large anharmonicity, just as observed in the case of formamide (*11*, *12*).

Because only the *a*-type *R* branches are observed for the vibrational satellites, the *B* and *C* constants are determined as listed in Table VIII, where the differences δB and δC, in the *B* and *C* constants, of the excited and ground states are included. It is interesting to note that for the ν_I satellite the difference $\delta B - \delta C$ is nearly the same, -6.5 to -7.0 MHz, for all the four isotopic species, whereas the sum $\delta B + \delta C$ changes drastically on the deuteration.

DISCUSSION

The N–C distance 1.358 ± 0.003 Å obtained in the present work is in agreement within experimental error with that in formamide, which is revised to be $1.35_2 \pm 0.012$ Å (*12*). The effect on the N–C bond length of replacing the oxygen atom by a sulfur atom is therefore not apparent. One might expect to obtain some information on the double-bond character of the N–C bond by analyzing the nuclear quadrupole coupling constant of ^{14}N. Unfortunately the present values of the coupling constant are not accurate enough to compare the double-bond character in the two molecules. The

TABLE VII. Observed Spectra and Vibrational Energies of the Excited States of Thioformamide

Transition	Normal	cis-D[a]	trans-D[a]	D_2
ν_I state				
$1_{01} \leftarrow 0_{00}$ (MHz)		11 257.6	10 875.3	10 550.4
$2_{12} \leftarrow 1_{11}$ (MHz)	22 755.9	21 911.3	21 277.1	20 572.0
$2_{02} \leftarrow 1_{01}$ (MHz)	23 295.8	22 508.7	21 747.3	21 096.3
$2_{11} \leftarrow 1_{10}$ (MHz)	23 845.5	23 117.7	22 224.1	21 629.8
E_v (cm^{-1})	393 ± 40			293 ± 30
ν_{II} state				
$1_{01} \leftarrow 0_{00}$ (MHz)	11 645.9	11 256.0	10 861.3	10 531.1
$2_{12} \leftarrow 1_{11}$ (MHz)	22 735.5	21 899.5	21 237.7	20 526.4
$2_{02} \leftarrow 1_{01}$ (MHz)	23 287.0	22 505.5	21 719.3	21 057.5
$2_{11} \leftarrow 1_{10}$ (MHz)	23 848.5	23 125.7	22 207.7	21 598.0
E_v (cm^{-1})	457 ± 50			393 ± 40

a. See footnote of TABLE I.

TABLE VIII. Rotational Constants of Thioformamide in the ν_I and ν_{II} States (MHz)

	Normal	cis-D[a]	trans-D[a]	D_2
ν_I State				
B_v	6097.5_0	5930.2_4	5674.3_8	5539.6_7
C_v	5552.7_0	5327.0_4	5200.8_8	5010.7_7
δB_v[b]	-4.2_4	-5.5_7	$+1.5_4$	$+2.9_5$
δC_v[b]	$+2.7_4$	$+0.9_7$	$+8.6_0$	$+9.8_7$
ν_{II} State				
B_v	6101.1_8	5934.6_1	5673.1_5	5533.4_4
C_v	5544.6_8	5321.5_0	5188.1_5	4997.6_4
δB_v[b]	-0.5_6	-1.2_0	$+0.3_1$	$+3.2_8$
δC_v[b]	-5.2_8	-4.5_7	-4.1_3	-3.2_6

a. See footnote of TABLE I.

b. Differences in the B and C constants of the excited and the ground state, i.e., $\delta B_v = B_v - B_0$ and $\delta C_v = C_v - C_0$.

larger dipole moment of thioformamide ($\mu_t = 4.01 \pm 0.03$ D) than that of formamide ($3.71_4 \pm 0.06$ D) (*10*) is also difficult to reconcile with a simple model based on the resonance forms depicted in Fig. 1.

The present data are not sufficient enough to draw a definite conclusion on the internal motion of the amino group. The spectral patterns of the amino wagging satellites are very similar to those of formamide, except that the fundamental frequencies are higher in thioformamide (393 cm^{-1}) than in formamide (295 cm^{-1}). For formamide the potential function of the amino wagging is of mixed quadratic and quartic without any potential hump at the planar configuration (*12*). The potential function in thioformamide therefore seems to be more quartic and the potential hump at the planar configuration is probably very small or completely absent.

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