Infrared Spectra and Normal Vibrations of Thioamides.
I. Thioformamide

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As has been reported in previous papers[1-3], the values of the Urey-Bradley type force constants for the simple primary and secondary amides, $HCONH_2$, CH_3CONH_2 and $HCONH\cdot CH_3$ were determined from their vibrational frequencies, and it was shown that these constants are transferable throughout the series of the molecules and that they give a good account of the nature of the normal vibrations of these molecules. About the vibrational spectra of the thioamides, on the other hand, few systematic investigations have yet been reported, and there are ambiguities in the assignments of many observed bands. As has been shown in the previous papers[1-3], all the values of the force constants necessary to calculate the normal vibrations of simple thioamides are now known except those concerning the sulfur atom. Therefore, the work has been extended to the thioamide group for the purpose of clarifying the nature of the normal vibrations of these molecules as well as to make a further check on the transferability of force constants of the Urey-Bradley type. The nature of the C=S and C–N bonds in thioamides is also discussed in connection with the force constants obtained. In the present paper, the results of infrared measurements and normal vibration calculations of thioformamide $HCSNH_2$, the first member of the series, are reported. The results for CH_3CSNH_2, $HCSNHCH_3$ and $CH_3CSNHCH_3$ will be given in subsequent papers.

Thioformamide and *N*-deuterated thioformamide were prepared, and their infrared spectra were measured in both liquid and solid states. The spectrum of $HCSNH_2$ in the liquid state corresponds well with that given earlier by Davies and Jones[4], except the band found at 439 cm^{-1} with medium intensity which was not reported. The assignments of the observed bands, however, differ considerably from theirs. The normal vibrations for thioformamide were first calculated with the force constants which were directly transferred from formamide[1] and thiourea[5]. Since the computed frequencies show a good agreement with the observed, the assignments of the infrared absorption bands can be made without difficulty. Then the values of the force constants were refined to obtain a better frequency fit. Based on the results of this calculation, the nature of the observed bands is explained in terms of the potential energy distributions and the vibrational amplitudes.

Experimental

Samples. — Thioformamide was prepared from formamide and P_2S_5 suspended in tetrahydrofuran[6] and was purified by the method shown in Ref. 7.

Exchange reaction with D_2O was employed to displace the amide hydrogen atoms by deuterium. Since thioformamide slowly decomposes at room temperature, the sample was mixed with a large

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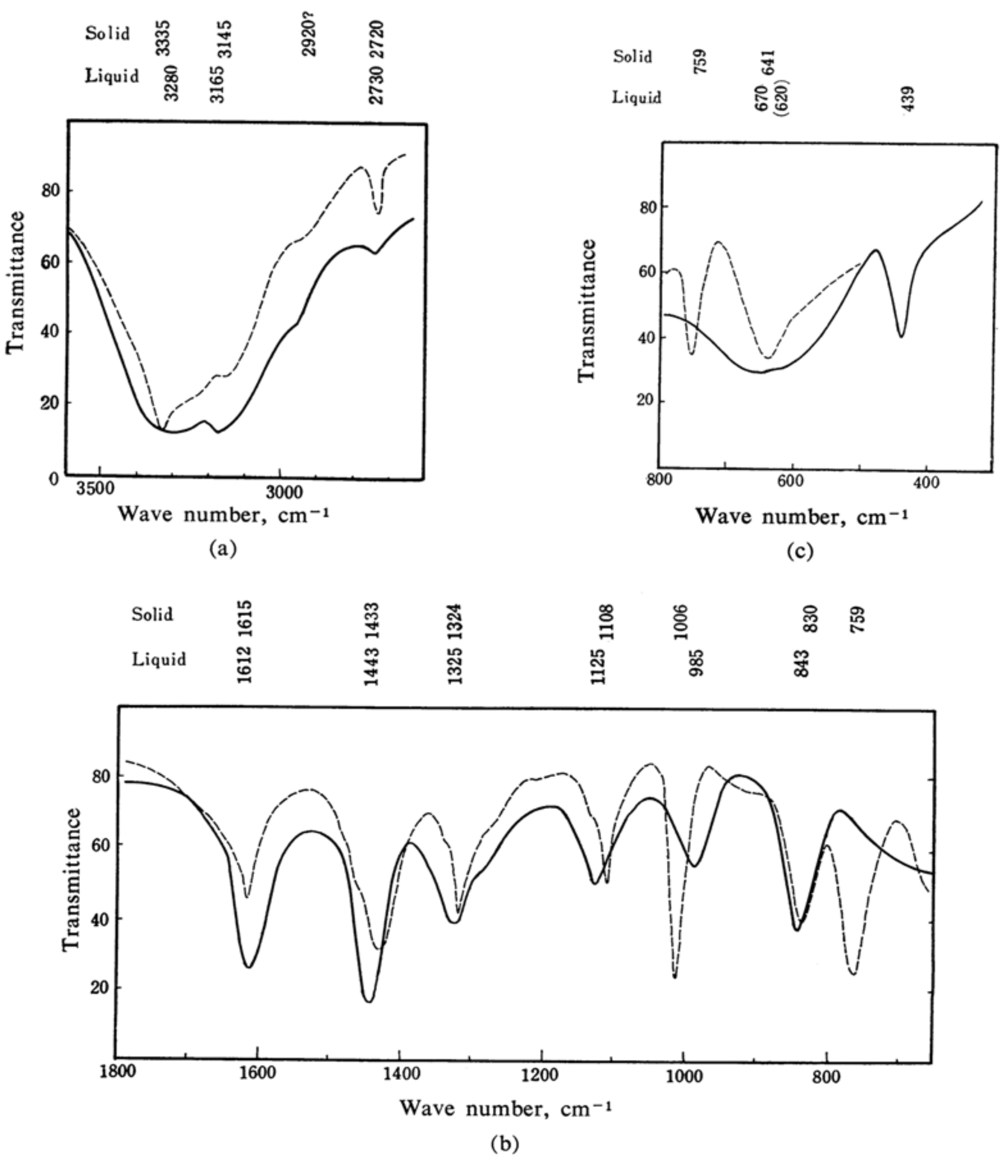
[1] I. Suzuki, This Bulletin, **33**, 1359 (1960).
[2] I. Suzuki, ibid., **35**, 540 (1962).
[3] I. Suzuki, ibid., **35**, 1279 (1962).
[4] M. Davies and W. J. Jones, *J. Chem. Soc.*, **1958**, 955.
[5] A. Yamaguchi, R. B. Penland, S. Mizushima, T. J. Lane, C. Curran and J. V. Quagliano, *J. Am. Chem. Soc.*, **80**, 527 (1958).
[6] S. Gabriel, *Ber. deut. chem. Ges.*, **49**, 1110 (1916).
[7] R. Willstäter and T. Werth, ibid., **42**, 1908 (1909).

excess of D_2O and shaken vigourously for a minute, and then the excess D_2O was quickly pumped out with a method analogous to freeze drying and measured immediately. Although thioformamide was reported to form monohydrate⁷⁾, no deuterium oxide seems to remain with the sample by this procedure; we did not detect the 1200 cm^{-1} band which is characteristic of D_2O.

Infrared Spectra.—The infrared spectra of these compounds were measured with a Hitachi EPI spectrophotometer equipped with sodium chloride optics, in the region from 4000 to 650 cm^{-1}, and with a Nippon Bunko grating spectrophotometer equipped with a cesium bromide foreprism in the region from 800 to 300 cm^{-1}. The solid state spectra were obtained with a low temperature cell⁸⁾ cooled with mixture of dry ice and methanol.

Infrared Spectra

The infrared spectra of $HCSNH_2$ in the liquid and solid states are shown in Figs. 1 (a)—(c), and those of $HCSND_2$, in Figs. 2 (a)—(c). As may be seen from Fig. 2, the spectra of the deuterated species are a little complicated by the presence of the bands arising from monodeuterated thioamides (HCSNHD,



(a) (c)

(b)

Fig. 1. Infrared spectra of $HCSNH_2$ in the liquid (solid line) and solid states (broken line). (a) 3600～2600 cm^{-1}, (b) 1800～650 cm^{-1}, (c) 800～300 cm^{-1}

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8) T. Miyazawa, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **76**, 821 (1955).

cis and trans) as well as of those from dideuterated species. When the sample was exposed to the atmosphere for a while, the former bands became strong in intensity as a result of the partial hydrogenation caused by the atmospheric vapor, while the latter became weak. In this way, the bands due to the NHD species could be identified. In Fig. 2, the bands whose wave numbers are given in parentheses are those arising from the NHD species.

Spectral changes due to the state of aggregation are sometimes very helpful in assigning the observed bands. In the case of $HCSNH_2$, changes in the spectra by solidification are not so significant as are those of formamide, and little change is observed in a number of vibration bands, including those chiefly associated with the NH_2 stretching, NH_2 bending, CN stretching and CH bending vibrations. However, the 985, 670 and 620 cm^{-1} bands in the liquid state change their positions considerably, and are found respectively at 1002, 759 and 641 cm^{-1} in the solid state. It will be shown in subsequent sections that these bands can reasonably be assigned to three out-of-plane (A'') vibrations: namely, the CH out-of-plane, NH_2 wagging and NH_2 twisting (CN torsional) vibrations; π(CH), $w(NH_2)$ and $t(NH_2)$.

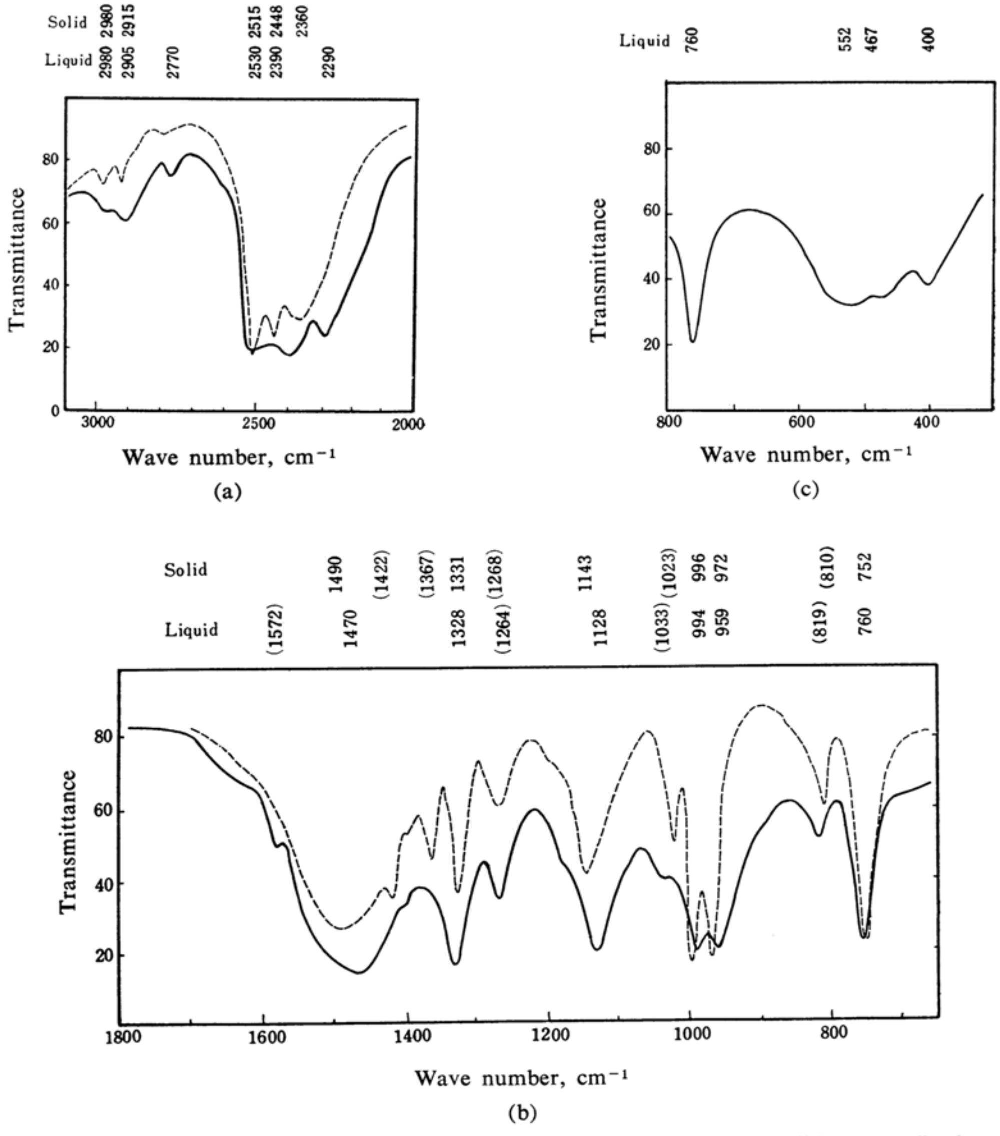

Fig. 2. Infrared spectra of $HCSND_2$ in the liquid (solid line) and solid states (broken line). (a) 3100~2000 cm^{-1}, (b) 1800~650 cm^{-1}, (c) 800~300 cm^{-1}

The difference in the strength of the NH···S hydrogen bonding between the solid and liquid states seems to be small, but the force field perpendicular to the molecular plane may be affected by solidification.

The assignment of the observed bands is chiefly based on the calculation of the normal vibration for $HCSNH_2$ and $HCSND_2$ molecules, so it will be discussed together with the results of that calculation.

Normal Coordinate Treatment

The calculation of the normal vibrations was made according to Wilson's method[9]. It was assumed that the molecule is planar, so the normal vibrations can be classified into 9 inplane (A′) and 3 out-of-plane (A″) vibrations. In the present paper the inplane vibrations are mainly treated[*1]. The structural parameters used in the present calculations are as follows, the bond lengths of $r(\mathrm{NH})=1.04\,\text{Å}$, $r(\mathrm{CH})=1.07\,\text{Å}$, $r(\mathrm{CN})=1.324\,\text{Å}$ and $r(\mathrm{CS})=1.713\,\text{Å}$. All the bond angles are assumed to be 120°[*2].

The symmetry coordinates used in the calculation are given in Table I.

Force Constants. — The potential function employed in the calculation is of the Urey-Bradley type[13]:

$$2V=\sum_i K_i(\Delta r_i)^2+\sum_{i\neq j} H_{ij}r_i^0 r_j^0(\Delta\alpha_{ij})^2+\sum_{i\neq j} F_{ij}(\Delta q_{ij})^2+\text{Linear terms}$$

where r_i and r_j are bond lengths with the equilibrium values r_i^0 and r_j^0; α_{ij}'s are bond angles, and q_{ij}'s, distances between nonbonded atoms. K, H, and F are stretching, bending and repulsive force constants respectively.

As has already been mentioned, the values of these force constants were first transferred from formamide[1] and thiourea[5][*3] they are given in the first column of Table II. The

TABLE I. SYMMETRY COORDINATES

S_i	$S=UR$	Vibrational mode	Abbr.
S_1	$(\Delta r_{\mathrm{NH_a}}-\Delta r_{\mathrm{NH_b}})/\sqrt{2}$	NH_2 antisym. stretching	$\nu_a(NH_2)$
S_2	$(\Delta r_{\mathrm{NH_a}}+\Delta r_{\mathrm{NH_b}})/\sqrt{2}$	NH_2 sym. stretching	$\nu_s(NH_2)$
S_3	Δr_{CH}	CH stretching	ν(CH)
S_4	Δr_{CN}	CN stretching	ν(CN)
S_5	Δr_{CS}	CS stretching	ν(CS)
S_6	$(2\Delta\alpha_{\mathrm{HNH}}-\Delta\alpha_{\mathrm{CNH_a}}-\Delta\alpha_{\mathrm{CNH_b}})/\sqrt{6}$	NH_2 bending	$b(NH_2)$
S_7	$(\Delta\alpha_{\mathrm{CNH_a}}-\Delta\alpha_{\mathrm{CNH_b}})/\sqrt{2}$	NH_2 rocking	$r(NH_2)$
S_8	$(2\Delta\alpha_{\mathrm{NCS}}-\Delta\alpha_{\mathrm{HCN}}-\Delta\alpha_{\mathrm{HCS}})/\sqrt{6}$	NCS bending	b(NCS)
S_9	$(\Delta\alpha_{\mathrm{HCN}}-\Delta\alpha_{\mathrm{HCS}})/\sqrt{2}$	CH bending	b(CH)
S_R'	$(\Delta\alpha_{\mathrm{HNH}}+\Delta\alpha_{\mathrm{CNH_a}}+\Delta\alpha_{\mathrm{CNH_b}})/\sqrt{3}$	Redundant	—
S_R''	$(\Delta\alpha_{\mathrm{NCS}}+\Delta\alpha_{\mathrm{HCN}}+\Delta\alpha_{\mathrm{HCS}})/\sqrt{3}$	Redundant	—

TABLE II. THE VALUES OF THE FORCE CONSTANTS (in md./A)

	I	II		I	II		I	II
K_{NH}	5.57^a	5.52	H_{HNH}	0.40^a	0.43	$F_{\mathrm{H\cdots H}}$	0^a	0
K_{CH}	3.74^a	3.88	H_{NHC}	0.32^a	0.27	$F_{\mathrm{N\cdots C}}$	0.46^a	0.46
K_{CN}	6.15_a	6.35	H_{NCH}	0.18^a	0.17	$F_{\mathrm{N\cdots H}}$	0.70^a	0.74
K_{CS}	3.50^b	3.95	H_{HCS}	0.18^c	0.13	$F_{\mathrm{H\cdots S}}$	0.70^c	0.60
			H_{NCS}	0.19^b	0.15	$F_{\mathrm{N\cdots S}}$	0.98^b	1.02

I: Initial set of the values
  a: transferred from $HCONH_2$
  b: transferred from $(NH_2)_2CS$
  c: assumed
II: Final set of the values

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9) E. B. Wilson, *J. Chem. Phys.*, 7, 1047 (1939); 9, 96 (1941).

[*1] Since the force field for the out-of-plane vibrations is quite different in nature from that for the in-plane vibrations, it is treated separately and will be reported on elsewhere, together with the results for other amides, such as $HCONH_2$, CH_3CONH_2, CH_3CSNH_2 and $HCSNHCH_3$ (see also Ref. 3).

[*2] No structural analysis has yet been reported for $HCSNH_2$, so the values of the C-N and C=S bonds are taken from those of CH_3CSNH_2[10], and the others from $HCONH_2$[11,12].

10) M. R. Truter, *J. Chem. Soc.*, **1960**, 997.

11) C. P. Post and J. Ladell, *Acta Cryst.*, **7**, 559 (1954).

12) R. A. Krombrout and G. B. Moulton, *J. Chem. Phys.*, **25**, 35 (1955).

13) T. Shimanouchi, ibid., **17**, 245, 734, 848 (1949).

[*3] The values adopted here are slightly different from those in Ref. 5. The present values are based on an unpublished work by Yamaguchi in which, starting with the values in Ref. 5, she obtained the values of the force constants to give the frequency fit with in 4% for all the bands of thiourea and deuterated thiourea.

TABLE III. THE OBSERVED AND CALCULATED FREQUENCIES, POTENTIAL ENERGY DISTRIBUTIONS; $(F_{ii}L_{is}^2/\lambda_s)\times 100$, AND PERCENT DEVIATIONS; $\Delta=(\nu_{\mathrm{obs}}-\nu_{\mathrm{calcd}})\times 100/\nu_{\mathrm{obs}}$

(a) $HCSNH_2$

	Frequency					P. E. D.								
	ν_{obs}	$\nu^{\mathrm{I}}_{\mathrm{calcd}}$	Δ^{I}	$\nu^{\mathrm{II}}_{\mathrm{calcd}}$	Δ^{II}	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9
ν_1	3287	3300	−0.2	3287	0.0	**101**	0*	0	0	0	0	0	0	0*
ν_2	3165	3204	−1.3	3191	−0.8	0*	**99**	0*	0*	0*	0*	0*	0*	0*
ν_3	(2905)	2872		2908		0	0	**102**	0*	0*	0	0	0	0
ν_4	1612	1620	−0.5	1623	−0.8	0*	1	0*	**20**	1*	**88**	0	0*	1*
ν_5	1443	1498	−4.0	1450	−0.5	0*	0	0*	44	11	8	2*	0*	**57**
ν_6	1325	1315	0.7	1308	0.5	0	0*	0*	**39**	0*	5*	4*	2*	**40**
ν_7	1125	1189	−5.6	1130	−0.5	0	0	0	0*	13*	0	**74**	8	6
ν_8	843	829	1.6	850	0.8	0	0*	1*	2	**81**	0*	17	5*	0
ν_9	439	451	−2.7	441	−0.5	0*	0	0	0	1	0*	4*	**90**	0

(b) $HCSND_2$

	ν_{obs}	$\nu^{\mathrm{I}}_{\mathrm{calcd}}$	Δ^{I}	$\nu^{\mathrm{II}}_{\mathrm{calcd}}$	Δ^{II}	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9
ν_1		2446		2434		**101**	0*	0	0	0*	0	1	0	0*
ν_2	2290	2317	−1.2	2307	−0.8	0	**98**	0	2*	0	1*	0	0	0*
ν_3	2905	2873	1.1	2908	−0.1	0*	0*	**102**	0*	0*	0	0	0	0
ν_4	1470	1507	−2.6	1477	−0.5	0*	1	0*	**74**	10*	8	0	0*	35*
ν_5	1328	1372	−3.4	1345	−1.3	0	1	0*	**16**	0	13	1*	1*	64
ν_6	1128	1110	1.6	1111	1.5	0*	1	0	9*	8	**74**	0*	0	3*
ν_7	994	1025	−3.1	1001	−0.7	0*	0*	0*	3	**43**	3*	**39***	19*	1*
ν_8	760	750	1.3	750	1.3	0	0	0*	2	**46**	1*	**48**	0	1
ν_9	400	414	−3.5	399	0.5	0*	0	1	0	0	0*	11*	**85**	0

* The asterisk means that the corresponding ***L***-matrix element is negative.

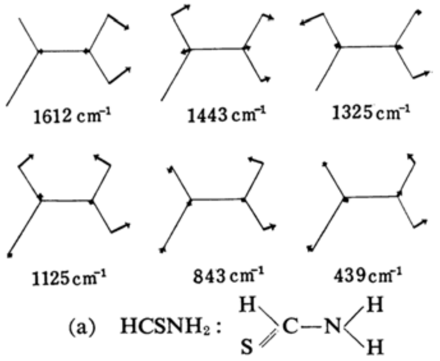
frequencies calculated from these values are given in the second column of Table III. As the force constants, H_{HCS} and $F_{\mathrm{H\cdots S}}$, for which few data were available, the values of 0.18 and 0.70 md./A respectively were assumed. Then the values of the force constants were refined to obtain a better frequency agreement. The final set of their values are given in the second column of Table II.

Results of Calculations.—With the values of the force constants given in the second column of Table II (Set II), the normal vibrations have been calculated. In Tables III (a) and (b), the observed and calculated frequencies, the percent deviations, and the potential energy distributions (P. E. D.) among the symmetry coordinates for each normal mode, as well as the signs of the corresponding L-matrix elements, are given. In Tables III (a) and (b), the calculated frequencies based on Set I of the force constants are also given for comparison.

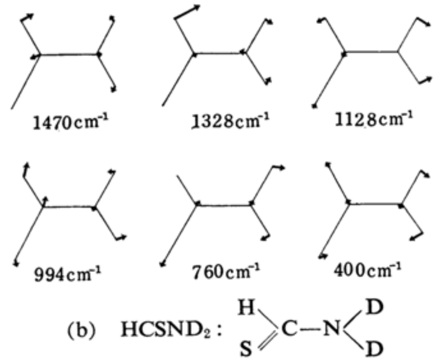
In order to visualize the features of the normal mode, it is preferable to compute the elements of the L^x matrix, which is defined, in matrix expression, as:

$$\boldsymbol{X}=\boldsymbol{L}^x\boldsymbol{Q}$$

where $\boldsymbol{X}$ is the column vector of the Cartesian coordinates of the atoms involved and $\boldsymbol{Q}$ is the normal coordinate vector. From the calculated values of the corresponding elements



(a) $HCSNH_2$:



(b) $HCSND_2$:

Fig. 3. The in-plane normal modes of thioformamides in Cartesian displacement vectors (A/unit change in normal coordinate).

of the L^x matrices, the vibrational feature of each normal mode is schematically shown in Figs. 3 (a) and (b) for both $HCSNH_2$ and $HCSND_2$. The features corresponding to the three higher frequencies are hydrogen (or deuterium) stretching vibrations and are obvious, so they are omitted from the figures.

The numerical computations were carried out with a PC-1 computer; the routines and the methods employed in the calculations have been described in detail in Refs. 14 and 15 and so are not discussed here.

Discussion

Force Constants.—As has been shown in the previous paper[1], the nature of the normal vibrations of the formamide molecule has been well elucidated from the simple Urey-Bradley force field without the terms $C_{ij}(\Delta q_{ij})^2$, which were used to refer to the repulsion between two nonbonded atoms situated at the cis position[16]. It has also been shown that the force constants obtained for $HCONH_2$ can be used without significant alteration in their values for $HCONHCH_3$ and CH_3CONH_2 molecules[2,3]. These facts suggest that the force field of this type can safely be applied in the study of thioamide groups, and that the force constants concerning the HC–NH_2 part of the molecule, at least as a starting set of values, may be assumed to be the same as those of formamide. A few additional data concerning the force constants involving the sulfur atom are transferred from thiourea.

The values of the force constants, Set I, of Table II, were determined in this way. As can be seen from Table II, the agreements between the observed and calculated frequencies, $\nu^{\mathrm{I}}_{\mathrm{calcd}}$, are far better than one might expect, the maximum deviation being 5.5% and the average, 2.2%. This shows that the assumption that was made was not far from the truth. The agreements are good enough to make the assignment of each observed band without ambiguities, except in the case of $HCSND_2$, which will be discussed later.

Once the assignment is settled, it is not difficult to refine the values of the force constants due to the indication given by the elements of the Jacobian matrix $(\delta\lambda_i/\delta K_j)$[17,18]. Such refinements were repeated, and the force constants given in the second column of Table II (Set II) were obtained. They give most of the calculated frequencies within 1% of the observed values; the maximum deviation is only 1.5%.

The values of some force constants are worth mentioning. The present calculation gives the value of K_{CN} to be 6.35 md./A, which is only 0.20 larger than that of $HCONH_2$. The value of K_{CN} is correlated closely with some repulsion force constants, such as $F_{\mathrm{H\cdots H}}$, $F_{\mathrm{H\cdots C}}$ and $F_{\mathrm{N\cdots S}}$ ($F_{\mathrm{N\cdots O}}$), and it is somewhat indefinite. However, it is sure that there is little difference between formamide and thioformamide in the nature of the C–N bond, and it has a considerable double bond character. Therefore, the value of K_{CS} obtained (3.95 md./A) should be considered to be much lower than that corresponding to the pure C=S bond[*4].

It is of interest to compare the values of $F_{\mathrm{H\cdots S}}$ and $F_{\mathrm{N\cdots S}}$ with those of $F_{\mathrm{H\cdots O}}$ and $F_{\mathrm{N\cdots O}}$ in $HCONH_2$. Although the sulfur atom has a larger van der Waals radius and is bulkier than the oxygen atom, the former values are about two-thirds of the latter. This is probably due to the much longer N···S or S···H distances. In this case, the distance between two non-bonded atoms becomes a dominant factor in determining the magnititudes of the repulsion constants.

Assignments of the Observed Bands.—For each in-plane normal vibration, the potential energy distributions among symmetry coordinates and Cartesian displacement vectors have been calculated; they are given, respectively, in Table III and Fig. 3. Based on these values, the qualitative assignments of the observed bands will be described.

The Bands above 2000 cm^{-1}.—The bands at 3280 and 3165 cm^{-1} of $HCSNH_2$ undoubtedly correspond to the $\nu_a(NH_2)$ and $\nu_s(NH_2)$ vibrations respectively. The band associated with the $\nu(CH)$ motion is found around 2900 cm^{-1}, but it is too weak for its precise position to be determined. The spectrum of $HCSND_2$ is rather complicated. The bands at 2530 and 2290 cm^{-1} might be associated with the $\nu_a(ND_2)$ and $\nu_s(ND_2)$, vibrations respectively, while the 2448 cm^{-1} is associated with the $\nu(ND)$ of the HCSNHD molecule. However, if these assignments were correct, the separation of the $\nu_a(ND_2)$ and $\nu_s(ND_2)$ frequencies is much larger than that of the $\nu_a(NH_2)$ and $\nu_s(NH_2)$

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14) T. Shimanouchi and I. Suzuki, *J. Mol. Spectroscopy*, **6**, 277 (1961).

15) T. Shimanouchi and I. Suzuki, ibid., **8**, 222 (1962).

16) D. E. Mann, T. Shimanouchi, J. H. Meal and L. Fano, *J. Chem. Phys.*, **27**, 43 (1957).

17) W. T. King, I. M. Mills and B. C. Crawford, ibid., **27**, 455 (1957).

18) T. Miyazawa, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **76**, 1132 (1955).

[*4] Truter suggests, from her recent X-ray investigation of thioacetamide, that the obtained values of 1.32 Å for the C-N bond length and 1.713 Å for the C-S bond length probably represent the lengths of the pure single C-N and double C-S bonds respectively[10]. However, the value of K_{CN} corresponding to the pure C-N bond is around 3.15~3.20 md./A[3,19]. The high values found in various amides and thioamides exclusively indicate the partial double bond character of the C-N bond.

19) A. Yamaguchi, ibid., **80**, 1105 (1959).

frequencies. This is highly improbable. In addition, the central peak is too strong in intensity and behaves somewhat differently from other peaks arising from the NHD species when the sample is exposed to atmospheric air. In the spectrum of $HCSNH_2$, a weak but well-defined band is found at 2454 cm^{-1}; this is probably due to the combination tone of the 1325 and 1125 cm^{-1} frequencies. In the N-dideuterated species, two bands are found at 1328 and 1128 cm^{-1}. Fermi resonance probably occurs between the $\nu_a(ND_2)$ vibration and the combination tone of the above two frequencies. This, as well as the coexistence of the $\nu(ND)$ band of HCSNHD, is the cause of the complexity of the spectrum. The unperturbed $\nu_a(ND_2)$ frequency is estimated as about 2450～2460 cm^{-1}.

The Band at 1612 cm^{-1}. — The band at 1612 cm^{-1} of $HCSNH_2$ can be assigned to an almost pure $b(NH_2)$ vibration; this is in agreement with the assignment by Davies and Jones[4]. In addition, there is small contribution of the $\nu(CN)$ mode. As seen in Fig. 3 (a), the C–N bond stretches when the HNH angle increases in this mode. In the deuterated species, the band corresponding to an almost pure $b(ND_2)$ vibration occurs at 1128 cm^{-1}. Contributions of the other vibrational modes to this band are found to be very small.

The Bands at 1443 and 1325 cm^{-1}.—Davies and Jones assigned the 1443 cm^{-1} band of $HCSNH_2$ to the $\nu(CN)$ vibration, and the 1325 cm^{-1} band to the $\delta(CH)$ vibration. The present calculations establish that these two vibrational modes couple with each other almost completely, and that each of the bands can not be assigned to a particular vibrational mode. The $\delta(CH)$ and $\nu(CN)$ vibrations also couple with each other in $HCONH_2$[1], but they are not so strong as in the case of $HCSNH_2$. The force constants H_{HCS} and $F_{H\cdots S}$ are smaller in value than H_{HCO} and $F_{H\cdots O}$ and lower the intrinsic frequency of the $\delta(CH)$ vibration, while that of the $\nu(CN)$ vibration increases as a result of the absence of the $\nu(CO)$ mode. This may be the cause of such a strong coupling. On deuteration, the band at 1443 cm^{-1} shifts towards higher frequencies by 27 cm^{-1}, while the 1325 cm^{-1} band scarcely moves.

The Bands at 1125 and 843 cm^{-1}.—The band at 1125 cm^{-1} $HCSNH_2$ is chiefly associated with the $r(NH_2)$ vibration, although there is a small contribution from the $\nu(CS)$ vibration. It is of general interest in the infrared investigation of thioamides to determine in what region the frequency characteristic of the $\nu(CS)$ mode appears. Various authors indicate various ranges for the $\nu(CS)$ vibration*5; e.g., 1500～1470 cm^{-1}, around 1300 cm^{-1}, around 1100 cm^{-1}, etc. In thiolactams, Mecke and Mecke assigned the bands around 1100 cm^{-1} to this mode[21]. In the case of $HCSNH_2$, Davies and Jones indicated that the interaction probably occurs between the $\nu(CS)$ and $\nu(CN)$ modes and gives rise to the two frequencies at 1443 and 1288 cm^{-1}. However, as may be seen from Fig. 1 (b), the 1288 cm^{-1} band is a weak shoulder of the strong 1325 cm^{-1} band, and, it can hardly be assigned to one of the fundamental frequencies. The present calculations show that the 843 cm^{-1} band of $HCSNH_2$ corresponds to an almost pure $\nu(CS)$ mode, while there is a small contribution from the $r(NH_2)$ vibration to this band. It is true that there are some difficulties in specifying tne characteristic C=S frequency as suggested by Davies and Jones. As will be shown in the subsequent papers, the $\nu(CS)$ vibration interacts with several vibrational modes in CH_3CSNH_2, $HCSNHCH_3$ and $CH_3CSNHCH_3$, and it is rather hard to tell which band is to be called the C=S stretching band. However, in the case of $HCSNH_2$, the band at 843 cm^{-1} corresponds to an almost pure $\nu(CS)$ vibration.

In *N*-dideuterated species, the vibrational interaction occurs between the $r(ND_2)$ and the $\nu(CS)$ modes; this gives rise to two observed frequencies at 994 and 760 cm^{-1}. Energetically, both the $\nu(CS)$ and $r(ND_2)$ vibrations contribute to these modes in approximately the same degree. The above facts suggest that the intrinsic frequency of the $\nu(CS)$ vibration lies in the region from 900 to 850 cm^{-1}.

Close to the 994 cm^{-1} band, another strong band is found in $HCSND_2$ at 959 cm^{-1}. This band is assigned to the $\pi(CH)$ vibration. It may be possible to reverse the assignment for these two bands. However, the present assignment is supported by the following evidence: (1) A band is found at 985 cm^{-1} in $HCSNH_2$ which is assigned to the $\pi(CH)$ mode without doubt. If we adopt the reverse assignment, the $\pi(CH)$ band would seem to shift towards a higher frequency on *N*-deuteration. This is quite improbable. (2) The 985 cm^{-1} band of $HCSNH_2$ shifts to a higher frequency by 21 cm^{-1} on solidification. The 959 cm^{-1} band of $HCSND_2$ also moves to a higher frequency by 13 cm^{-1}, while the 994 cm^{-1} band shifts very little*6. (3) The computed frequency always favors the present assignment.

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*5 As a summary of the $\nu(CS)$ frequency, see Ref. 20, p. 350.

20) L. J. Bellamy, "The Infrared Spectra of Complex Molecules", Methuen & Co., Ltd., London (1958), p. 350.

21) R. Mecke and R. Mecke Jr., *Ber. deut. chem. Ges.*, 89, 343 (1959).

*6 In $HCONH_2$[8], and in $HCONHCH_3$[3], the bands associated with the $\pi(CH)$ mode shift towards higher frequencies on solidification.

The Band at 439 cm^{-1}.—Present calculation shows this band arises from the δ(NCS) vibration and corresponds well with the 412 cm^{-1} band of thiourea[5]. On *N*-deuteration, the r(ND_2) vibration interacts with the δ(NCS_2) mode and lowers the band by 39 cm^{-1}. This is in good agreement with the calculated shift.

The Out-of-plane (A$''$) Vibrations.—Once the assignments for the in-plane normal vibrations are settled, it is not difficult to pick up the bands associated with the out-of-plane vibrations. In $HCSNH_2$, they are found at 985, ca. 670 and ca. 620 cm^{-1}. The absorption around 650 cm^{-1} in the liquid spectrum is very broad, and it is difficult to judge whether it is due to a single, very broad band or to two broad bands overlapping each other. The inspection of the spectrum taken in the solid phase shows that the latter is the case. It gives two distinct bands at 641 and 759 cm^{-1}. The 985 cm^{-1} band is assigned to the π(CH) vibration without ambiguity, while the bands at 670 (759) and 620 (641) cm^{-1} are assigned to the w(NH_2) and t(NH_2) vibrations respectively. The t(NH_2) vibration is closely associated with the nature of the C–N bond, since it should accompany the torsional movement around the C–N bond. The bands at 1443 and 1325 cm^{-1}, which are associated with the ν(CN) vibration, are insensitive to solidification; therefore, the band less sensitive to solidification is chosen as due to the t(NH_2) vibration. In $HCSND_2$, the band found at 959 cm^{-1} is assigned to the π(CH) vibration, as has been described above. The bands corresponding to the w(ND_2) and t(ND_2) vibrations are found at 552 cm^{-1} and 467 cm^{-1} respectively.

Thus complete assignments for the observed bands of both the $HCSNH_2$ and $HCSND_2$ molecules have been made. The present assignment for the $HCSNH_2$ molecule considerably differs from that made by Davies and Jones. However, this assignment is supported firmly by the calculations of the normal vibrations and by the change in the spectrum due either to *N*-deuteration or to solidification.

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