Infrared Spectra and Normal Vibrations of Thioamides.
II. Thioacetamide

By Isao SUZUKI

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In a preceding paper (hereafter refered to as (I))[1], the results of a normal coordinate analysis of thioformamide, the first member of the thioamide group, as well as its *N*-deuterated analogue, were reported on. It was shown in (I) that the Urey-Bradley force field[2] can be applied to the $HCSNH_2$ molecule successfully, and that it gives a very good account of the nature of the normal vibrations of the molecule. As a continuation of that research, an analysis of the vibrational spectra of thioacetamide and *N*-dideuterated thioacetamide has now been made; the results will be given in the present paper.

The Raman and infrared spectra of thioacetamide have been studied by several investigators[2-7] and the assignments of some vibration bands have been reported. Recently Kutzelnigg and Mecke studied the infrared spectra of thioacetamide and its complexes and presented assignments for the observed frequencies[7]. In order to make a detailed analysis of the nature of normal vibrations and to determine the values of the force constants more precisely, it is vitally important to investigate the spectrum of CH_3CSND_2 as well as that of CH_3CSNH_2. Therefore, *N*-dideuterated thioacetamide was prepared, and the infrared spectra of both CH_3CSNH_2 and CH_3CSND_2 were measured in the solid and liquid states and in solutions. A normal coordinate treatment for the in-plane vibrations of these molecules was undertaken, the Urey-Bradley force field being employed in the calculations.

Experimental

Sample.—Thioacetamide (CH_3CSNH_2) was obtained from a commercial source and was purified by recrystallization from chloroform; m. p., 110.5°C (uncorr.).

Exchange reaction with deuterium oxide was employed to prepare *N*-dideuterated thioacetamide (CH_3CSND_2); thioacetamide was mixed with excess D_2O and was heated until it was completely dissolved in D_2O. Then the solution was cooled and the excess D_2O was pumped out in vacuum; this procedure was repeated until the NH stretching bands around 3200 cm^{-1} became almost undetectable.

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[1] I. Suzuki, This Bulletin, **35**, 1286 (1962).

[2] T. Shimanouchi, *J. Chem. Phys.*, **17**, 245, 734, 848 (1949).

[3] K. W. F. Kohlrahsch and J. Wagner, *Z. physik. Chem.*, **B45**, 229 (1940).

[4] R. Mecke and H. Speisecke, *Chem. Ber.*, **89**, 1110 (1956).

[5] E. Spinner, *Spectrochim. Acta*, **15**, 95 (1959).

[6] L. J. Bellamy and P. Z. Rogasch, *J. Chem. Soc.*, **1960**, 2218.

[7] W. Kutzelnigg and R. Mecke, *Spectrochim. Acta*, **17**, 530 (1961).

TABLE I. OBSERVED FREQUENCIES (IN cm^{-1}) OF THIOACETAMIDES

(a) CH_3CSNH_2

Solid	Liquid	Solution			Assignment
		CS_2	$CHCl_3$	CH_3CN	
3290	3305	3515	3496	3440	$\nu_a(NH_2)$
3165	3160	3391	3381	3230	$\nu_s(NH_2)$
2945	2948		2962		$\nu_a(CH_3)$
2860					
2670					
2620	2613				
1648	1627		1606	1632	$b(NH_2)$
1478	1472				$\delta_a(CH_3)$
1393	1400 br.	1425 (CCl_4)			$\nu(CN)$
1364	1364	1357	1367		$\delta_s(CH_3)$
1306	1302	1315	1316	1309	Skeletal$+r(NH_2)$
1030	1020				$r(NH_2)+r(CH_3)$
975	970	967	966	975	$\nu(CC)+r(CH_3)+\nu(CS)$
718	715			719	$\nu(CS)+\nu(CC)$
709	625 br.			650 br.	$w(NH_2)$ and $t(NH_2)$
517	512			511	$\pi(CC)$
471 460	448			445	$\delta(NCS)$
375	373				$\delta(CC)$

(b) CH_3CSND_2

Solid	Liquid	Solution			Assignment
		CS_2	$CHCl_3$	CH_3CN	
	(2960)				$\nu_a(CH_3)$?
	2925				$\nu_s(CH_3)$
2470	2540	2622	2612	2580	$\nu_a(ND_2)$
2340	2390	2465	2461	2425	$\nu_s(ND_2)$
1500 1495			1488		$\delta_a(CH_3)+\nu(CN)$
1423	1400 br.				$\nu(CN)+\delta_a(CH_3)$
1365	1369	1346	1365		$\delta_s(CH_3)$
1238	1238	1249	1250	1244	Skeletal$+r(ND_2)$
1160	1158			1166	$b(ND_2)$
1075					
	1050				$r(CH_3)$ (A''?)
1025					
981	981		982	984	$r(CH_3)$
	865			867	
838	826			828	$\nu(CC)+r(ND_2)$
699 694	695			703	$\nu(CS)$
580					
556	552			553	$w(ND_2)$ $t(ND_2)$ $\pi(CC)$
521					
478	479 br.			476	
	452 br.			454	
427	415			405	$\delta(NCS)$
374	374			(368)	$\delta(CC')$

Infrared Spectra.—The infrared spectrophotometers used in the present work were the same as described in (I), and the measurements were made in the region from 3500 to 300 cm^{-1}. The spectra in the solid state were measured as Nujol or hexachlorobutadiene mulls; they are given in Figs. 1 (a)—(c). Those in the liquid state were obtained by heating samples between KCl or KRS-5 plates to slightly above the melting point with a heater embedded between two thin mica plates*[1]. Acetonitrile, chloroform and carbon disulfide were used as solvents for the measurements in solutions. Owing to the low solubility of the sample in nonpolar solvents, the measurements were made with a variable thickness cell with a thickness up to 5 mm. The results of these measurements are summarized in Tables I (a) and (b).

Normal Coordinate Treatment

The normal vibrations were calculated as a nine-body problem, assuming a planar structure for the molecule similar to that of acetamide. The procedures of the calculation are quite analogous to those for the acetamide molecule[8], so they are not described here. The

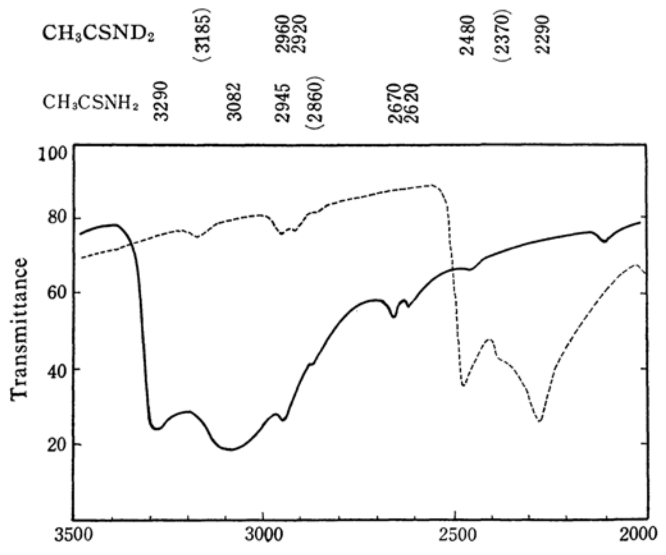

Fig. 1 (a)

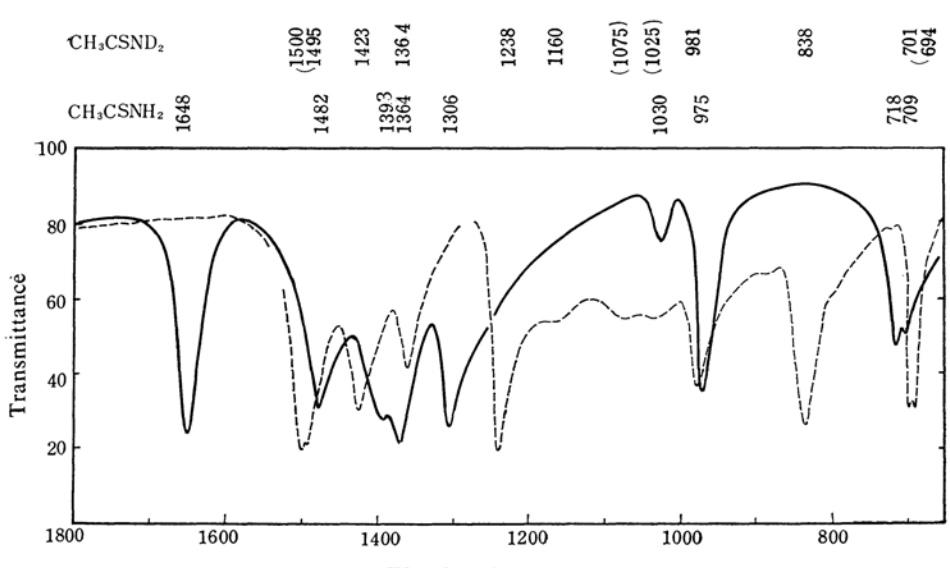

Fig. 1 (b)

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*[1] Since thioacetamide is less stable under these conditions, the positions of the observed bands were determined by repeating the measurements several times.

8) I. Suzuki, This Bulletin, 35, 1279 (1962).

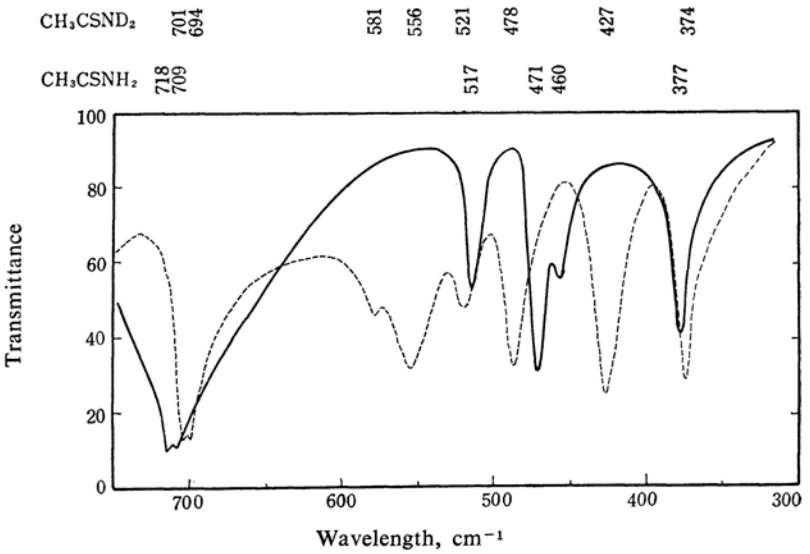

Fig. 1 (c)

Fig. 1. Infrared spectra of CH$_3$CSNH$_2$ (solid line) and CH$_3$·CSND$_2$ (broken line) in the solid state.
(a) 3500~2000 cm^{-1}, (b) 1800~650 cm^{-1}, (c) 800~300 cm^{-1}

structural parameters used are the bond lengths of r(C=S) = 1.713 Å, r(C–N) = 1.324 Å, r(C′C)*[2] = 1.494 Å, r(N–H) = 1.02 Å and r(C–H) = 1.09 Å, and the bond angles of 120° for those around the C and N atoms and of 109°47′ for those around the C′ atom[9),*3]. The symmetry coordinates used are listed in Table II.

TABLE II. SYMMETRY COORDINATES*

S_i	Vibrational Modes	Abbr.
S_1	CN stretching	ν(CN)
S_2	CC′ stretching	ν(CC)
S_3	CS stretching	ν(CS)
S_4	NH$_2$ bending	b(NH$_2$)
S_5	NH$_2$ rocking	r(NH$_2$)
S_6	NCS deformation	δ(NCS)
S_7	CC′ deformation	δ(CC′)
S_8	CH$_3$ asym. deformation	δ_a(CH$_3$)
S_9	CH$_3$ sym. deformation	δ_s(CH$_3$)
S_{10}	CH$_3$ rocking	r(CH$_3$)

* Higher frequencies are separated from lower frequencies[10,11)]. Combinations of the internal coordinates in each symmetry coordinate are shown in Ref. 8.

All the numerical computations were carried out with a parametron computer, PC-1. The methods and the routines used in the present study are the same as those described in Refs. 12 and 13.

Results and Discussion

Force Constants.—A considerable amount of data has now been accumulated on the values of the Urey-Bradley force constants for simple amides and thioamides; this is summarized in Table III. It is not difficult to select an appropriate set of force constants for this molecule. The normal vibrations were first calculated from the constants mainly transferred from HCSNH$_2$[1)] and CH$_3$CONH$_2$[8)]; then the values of the constants were refined so as to obtain a better frequency fit. The final set of these values are given in the last column of Table III.

The force constants listed in Table III can be roughly classified into two groups: (A) the constants involving the sulfur or oxygen atoms, and (B) those concerned with other atoms. As was pointed out in (I), the repulsive force constants involving the sulfur atom are found to be always smaller than the corresponding constants involving the oxygen atom. This is also the case for the stretching,

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[*2] C and C′ denote the thiocarbonyl and methyl carbon atoms respectively.

9) M. Truter, *J. Chem. Soc.*, **1960**, 997.

[*3] The bond lengths are based on recent X-ray investigation of thioacetamide[9)]. The bond angles are assumed, for the sake of simplicity, to be tetrahedral and 120°; these values are not, however, far from the reported values.

10) E. B. Wilson, *J. Chem. Phys.*, **7**, 1047 (1939); **9**, 76 (1941).

11) E. B. Wilson, J. C. Decius and P. C. Cross, "Molecular Vibrations", McGraw-Hill Co., New York (1955), p. 74.

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

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

TABLE III. FORCE CONSTANTS OF AMIDES AND THIOAMIDES, (md./A)*,**

	$HCONH_2$	$HCSNH_2$	$HCONHCH_3$		CH_3CONH_2	CH_3CSNH_2	
K_{NH}	5.80	5.52					
K_{CH}	3.74	3.88					
K_{CX}	8.80	**3.95**	8.80		8.50	**3.40**	
K_{CN}	6.15	6.35	6.15		5.75	5.70	
H_{HNH}	0.40	0.43			0.40	0.41	
$F_{H\cdots H}$	0	0			0	0	
H_{HNC}	0.32	0.27	0.30		0.32	0.32	
$F_{H\cdots C}$	0.46	0.46	0.46		0.46	0.44	
H_{HCN}	0.18	0.17	0.18	H_{CCN}	0.30	0.27	
$F_{H\cdots N}$	0.70	0.74	0.72	$F_{C\cdots N}$	0.70	0.68	
H_{HCX}	0.20	**0.13**	0.20	H_{CCX}	0.32	**0.27**	
$F_{H\cdots X}$	0.92	**0.60**	0.92	$F_{C\cdots X}$	0.72	**0.44**	
H_{NCX}	0.34	**0.15**	0.37		0.34	**0.24**	
$F_{N\cdots X}$	1.50	**1.02**	1.50		1.50	**1.17**	
$K_{C'N}$			3.15	K_{CC}	2.40	2.70	N-CH_3 or C-CH_3 part
H_{HCH}			0.43		0.43	0.43	
$F_{H\cdots H}$			0.03		0.05	0.05	
$H_{HC'N}$			0.28	H_{HCC}	0.25	0.25	
$F_{H\cdots N}$			0.52	$F_{H\cdots C}$	0.47	0.50	
κ (md.·A)			−0.04		−0.05	−0.05	
$F' = -F/10$							

* The definitions of K, H and F are the same as in (I), κ is an intramolecular tension defined by Shimanouchi[2].

** X denotes oxygen or sulfur atom. In this table, values of the force constants associated with the sulfur atom are given in bold-faced letters.

and bending force constants*4. The force constants belonging to (B) show excellent transferability throughout the series of thioamides as well as that of amides. The nature of the NH_2, CN and CH_3 groups seems to be scarcely affected by the substitution for the oxygen of the sulfur atom.

The repulsive force constants $F_{N\cdots S}$ are found to be comparatively large, as in the case of $F_{N\cdots O}$. The Urey-Bradley type force field does not contain resonance terms such as $k_{NS}(\Delta r_{CS})\cdot(\Delta r_{CN})$ explicitly, where K_{NS} is a force constant. Therefore, the value of $F_{N\cdots S}$ is partly affected by the resonance force constant k_{NS} and is somewhat effective.

Assignments of the Observed Bands. — The computed frequencies given in Tables IV (a) and (b) are obtained from the force constants listed in the final column of Table III, and correspond to the observed frequencies very closely. Therefore, the potential energy distributions among the symmetry coordinates given in Tables IV (a) and (b) can be considered to represent the quantitative assignments of the observed frequencies. In order to visualize the normal vibration modes corresponding to these vibration bands, the Cartesian displacement vectors have also been calculated*5; they are illustrated in Figs. 2 (a) and (b). Based on the results of calculation, the nature of some vibration bands characteristic of the thioamide group is discussed in this section.

As has been pointed out by Kutzelnigg and Mecke, one of the difficulties in interpreting the spectrum of thioacetamide is the complexity of the spectrum in the region from 1500 to 1300 cm^{-1}. However, the present calculation gives a good account of the nature of these bands. Among the four bands observed in this region, the 1364 cm^{-1} band can reasonably

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*4 It is interesting to note that the ratio of K_{CO}/K_{CS} obtained from carbon dioxide and carbon disulfide (K_{CO} =15.5, K_{CS}=7.5) is close to the value obtained here[14].

14) Ref. 11, p. 311.

*5 In the present calculation, the CH and NH stretching frequencies are separated from the lower frequencies. Therefore, care should be taken in calculating the L^X matrix, which is usually obtained by equation 1.

$$L^X = M^{-1}B'G^{-1}L \qquad (1)$$

Miyazawa and the author have found that the process for higher frequency separation is equivalent to transforming G into $G^* = TGT'$, where G, G^* and T have the following expressions, if we adopt Wilson's notation[14]:

$$G = \begin{Vmatrix} G_{11} & G_{12} \\ G_{21} & G_{22} \end{Vmatrix}, \quad G^* = \begin{Vmatrix} G_{11} & 0 \\ 0 & G_{22} - G_{21}G_{11}^{-1}G_{12} \end{Vmatrix}$$

$$\text{and } T = \begin{Vmatrix} E_{11} & 0 \\ -G_{21}G_{11}^{-1} & E_{22} \end{Vmatrix}.$$

Instead of Eq. 1, one should employ the following equation for obtaining the L^X matrix:

$$L^X = M^{-1}B'T'G^{*-1}L \qquad (2)$$

TABLE IV. THE OBSERVED AND CALCULATED FREQUENCIES, PERCENT DEVIATIONS, AND POTENTIAL ENERGY DISTRIBUTIONS AMONG THE SYMMETRY COORDINATES, $(F_{ii}L_{is}^2/\lambda_s)\times 100$

(a) CH_3CSNH_2

Q_i	ν_{obs}	ν_{calcd}	$\Delta\nu$*	Δ*	P. E. D.									
					S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9	S_{10}
Q_1	1648	1634	+14	0.8	13	0	0	**93**	0	0	0	0	0	0
Q_2	1482	1478	+ 4	0.3	9	0	2	2	0	0	1	**68**	0	**16**
Q_3	1393	1396	− 3	0.2	**62**	5	4	**5**	0	3	7	16	6	1
Q_4	1364	1374	−10	0.7	4	10	1	0	0	0	1	1	**99**	0
Q_5	1306	1310	− 4	0.3	0	**26**	**17**	0	**50**	**15**	6	2	0	2
Q_6	1030	1028	+ 2	0.2	4	12	4	0	**29**	1	2	8	0	**46**
Q_7	975	964	+11	1.1	9	**34**	**14**	0	**16**	2	0	4	0	**28**
Q_8	718	718	0	0	5	**16**	**57**	0	1	0	6	1	0	3
Q_9	471	468	+ 3	0.7	0	3	2	0	4	**76**	8	0	0	0
Q_{10}	377	388	+11	2.9	1	2	8	0	0	11	**73**	1	0	3

(b) CH_3CSND_2

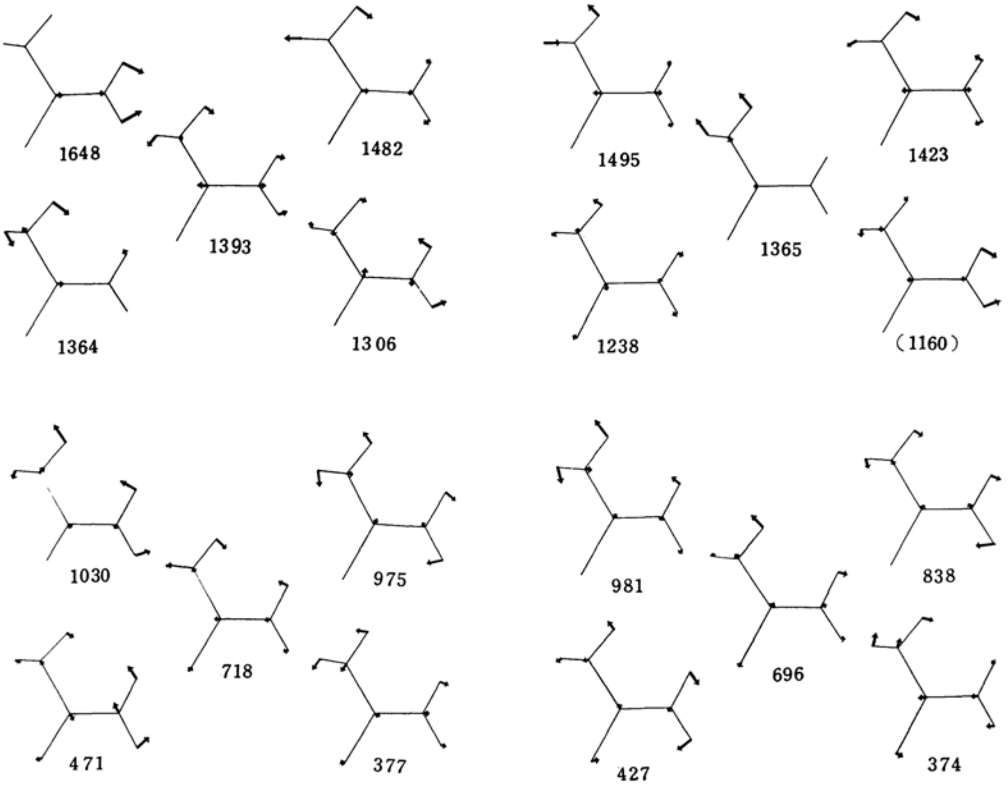
Q_i	ν_{obs}	ν_{calcd}	$\Delta\nu$*	Δ*	P. E. D.									
					S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8	S_9	S_{10}
Q_1	1495	1487	+ 8	0.6	**28**	1	3	3	0	0	2	**50**	0	16
Q_2	1423	1431	− 8	0.6	**54**	5	2	10	0	2	5	**35**	1	0
Q_3	1364	1374	−10	0.7	1	9	0	0	0	0	0	0	**104**	0
Q_4	1238	1231	+ 7	0.6	0	**43**	**28**	0	**21**	**19**	6	3	0	6
Q_5	(1160)	1179	—	—	1	5	2	77	0	1	4	2	0	8
Q_6	981	978	+ 3	0.3	12	1	4	6	4	1	0	9	0	**65**
Q_7	838	836	+ 2	0.2	3	31	3	1	57	1	1	0	0	0
Q_8	696	702	− 6	0.9	6	9	**58**	3	6	0	6	0	0	3
Q_9	427	433	− 6	1.4	0	1	1	0	**12**	**66**	**14**	0	0	1
Q_{10}	374	362	+12	3.2	1	4	7	0	0	**18**	**62**	1	0	2

* $\Delta\nu=\nu_{obs}-\nu_{calcd}$, $\Delta=|\Delta\nu|/\nu_{obs}$

be assigned to an almost pure $\delta_s(CH_3)$ vibration. Of the remaining three, the 1482 cm^{-1} band is found to be chiefly associated with the $\delta_a(CH_3)$ vibration, while the band at 1392 cm^{-1}, with the ν(CN) vibration, although a coupling between these two vibrational modes takes place. In the *N*-dideuterated species, the coupling occurs more strongly than in the normal species; this gives rise to two observed bands at 1495 and 1423 cm^{-1}.

The present calculations show that the nature of the 1306 cm^{-1} band of CH_3CSNH_2 is very complicated and that it cannot be attributed to one or two vibration modes. This may be the cause of the difficulty in interpreting the nature of this band. The $r(NH_2)$, ν(CC), ν(CS) and δ(NCS) vibrations contribute to this band. As may be seen from Fig. 2 (a), this normal vibration involves the rocking motion of the NH_2 group as well as the movements of the two carbon atoms perpendicular to the C–N bond and antiparallel to each other. In the *N*-dideuterated species, the band found at 1238 cm^{-1} corresponds to this normal mode, although the contribution of the $r(NH_2)$ motion to this mode decreases considerably, while that of the ν(CC) vibration increases.

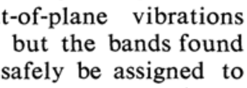
The band at 1030 cm^{-1} is assigned to the hybridized vibration containing the $r(NH_2)$ and $r(CH_3)$ vibrations, and these two vibrations also contribute to the 975 cm^{-1} band. It is of interest to seek in which region the band chiefly associated with the ν(CS) vibration appears. In the case of $HCSNH_2$, it was found that the band at 843 cm^{-1} corresponds to an almost pure ν(CS) vibration. In thioacetamide, the situation is rather complicated by the existence of the C–C bond adjacent to the C=S bond. The ν(CC) and ν(CS) vibrations are coupled with each other. In fact, the normal vibrations at 1306, 975 and 718 cm^{-1} of CH_3CSNH_2 involve considerable contributions from the ν(CC) and ν(CS) vibrations. Above all, the contribution of the ν(CS) vibration to the 718 cm^{-1} band is comparatively large; the energy associated with this motion is about 60% of the total. This is consistent with the fact reported by Kutzelnigg and Mecke that this band is shifted by 29 cm^{-1} toward a lower frequency on the



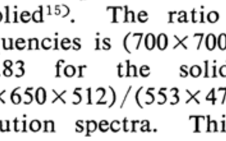
(a) (b)

Fig. 2. The normal modes of CH_3CSNH_2 and CH_3CSND_2 in Cartesian displacement vectors projected to the molecular plane. (A/unit change in normal coordinate)

(a) CH_3CSNH_2:



(b) CH_3CSND_2:



formation of a complex with cupper chloride[7].

In the region below 800 cm^{-1}, the bands of CH_3CSNH_2 found at 471 and 377 cm^{-1} are assigned to two skeletal deformation vibrations. The spectrum of CH_3CSND_2 is complicated, since some out-of-plane vibrations also occur in this region, but the bands found at 427 and 374 cm^{-1} can safely be assigned to these deformation vibrations. The approximate assignment of each observed band is given in the last column of Tables I (a) and (b).

Three out-of-plane (A'') vibrations are expected to appear in the region below 800 cm^{-1}. They are the NH_2 wagging, NH_2 twisting and CC out-of-plane bending vibrations, $w(NH_2)$, $t(NH_2)$ and π(CC) ; the assignments for these modes are also included in Tables I (a) and (b). The present assignments are based on the fact that the out-of-plane vibrations are sensitive to change in the states in which the substance is measured. In order to check the assignments of the out-of-plane vibrations, the product rule is applied[15]. The ratio of the three observed frequencies is $(700\times700\times517)/(556\times476\times454)=1.83$ for the solid state spectra[*6], and $(650\times650\times512)/(553\times476\times454)=1.81$ for the solution spectra. This is in good agreement with the theoretical value of 1.83_2.

A more detailed analysis of the out-of-plane vibrations is now in progress for various

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[*6] The $w(NH_2)$ and $t(NH_2)$ frequencies appear around 700 cm^{-1}. In $HCSNH_2$, they occur at 670 and 620 cm^{-1} in the liquid state and at 754 and 645 cm^{-1} in the solid state (I). Although we cannot resolve the absorption around 700 cm^{-1}, it seems reasonable to assume that these vibrations happen to be at approximately the same frequency. It should be emphasized that three distinct bands are found at 769, 735 and 690 cm^{-1} in the spectrum of the CH_3CSNH_2-CuCl complex[7].

amides and thioamides; the results will be published elsewhere.

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Department of Chemistry
Faculty of Science
The University of Tokyo
Hongo, Tokyo