192. *The Infrared Spectrum of Thioformamide.*

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The spectrum of thioformamide has been studied from 400 to 5000 cm.$^{-1}$. No indications of any form other than that of the amide structure, $\mathrm{H{\cdot}C(:S){\cdot}NH_2}$, were detected, although there is strong hydrogen-bond association in the liquid state. The assignment of the twelve fundamental frequencies is considered and, in relation to the recognition of a $\nu(\mathrm{C{=}S})$ mode, the limitations of the concept of " characteristic bond frequencies " are emphasised.

There has been frequent and detailed discussion of the vibrational spectra of the amides, but far fewer accounts of the thioamide spectra are available and there is uncertainty as to the assignment of what might be expected as the characteristic frequencies of the $\mathrm{S{=}C{-}N}$ group. Accordingly we have studied thioformamide, the first member of the series $\mathrm{R{\cdot}C(:S){\cdot}NH_2}$, although it will not necessarily be typical of the group. No systematic account of its infrared or Raman spectrum appears to have been published.

Experimental

Thioformamide, prepared by Gabriel's method [1] and purified as by Willstätter and Wirth,[2] had m. p. 28—29° (lit., 29°). The solid shows obvious signs of decomposition if kept at room temperatures for about ½ hr.; in diethyl ether solution it may be kept for much longer (preferably below room temperature) without decomposition. It is only sparingly soluble in solvents suitable for determination of infrared spectra, but by means of a double-beam spectrometer numerous features of the spectra from 2 to 15 μ were recorded in a 0·11 mm. cell for MeCN solutions and in a 2·5 mm. cell for $\mathrm{CCl_4}$ solutions; for the latter solvent cells up to 4 cm. thickness could be used in the 3 μ region.

Liquid films were examined from 2 to 25 μ. They were prepared as follows: (i) by evaporation of an ethereal solution on a rock-salt plate, producing a solid film which, when covered with a second plate and placed in the radiation beam, became a liquid film; (ii) a little solid thioformamide precipitated from ethereal solution by light petroleum was placed between rock-salt plates and melted by warming. The spectra thus obtained were identical and no features ascribable to hydrogen sulphide formed on decomposition could be detected in the records. From 2 to 15 μ spectra were obtained on a Grubb-Parsons double-beam grating spectrometer (G.S.2) and from 15 to 25 μ on a Grubb-Parsons single-beam (S.3) instrument with a potassium bromide prism.

Results and Discussion

Analogously to the position with amides, a tautomeric imino-form, $\mathrm{HS{\cdot}CH{:}NH}$, has on occasions been suggested for thioformamide. In the spectra we failed to detect any trace of a $\nu(\mathrm{SH})$ absorption or of any other features suggesting the presence of a tautomer. Accordingly, assuming the amino-form of the molecule, we can describe the twelve fundamental vibrational modes in the following approximate terms: $\nu_a(\mathrm{NH_2})$: $\nu_s(\mathrm{NH_2})$: the in-plane bending mode $\delta(\mathrm{NH_2})$: $\nu(\mathrm{C{-}H})$: the two deformation modes $\delta(\mathrm{CH})$ and $\gamma(\mathrm{CH})$ respectively within and perpendicular to the (NCS) plane: $\nu_a(\mathrm{NCS})$: $\nu_s(\mathrm{NCS})$: $\delta(\mathrm{NCS})$: and, on the assumption of an all-planar form of the molecule, an in-plane rocking motion of the $(\mathrm{NH_2})$ group, $r(\mathrm{NH_2})$: the in-phase out-of-plane motion of the two hydrogen atoms which may be designated wagging $(\mathrm{NH_2})$: and the out-of-phase version of the same displacements which is a twisting $(\mathrm{NH_2})$. The wave numbers of the absorptions observed together with estimated relative intensities are given in Table 1.

Apart from features arising from associated molecules, the $\mathrm{CCl_4}$ solutions show in the 3 μ region three major absorption centres, at 3495, 3374, and 2965 cm.$^{-1}$. These are respectively, $\nu_a(\mathrm{NH_2})$, $\nu_s(\mathrm{NH_2})$, and $\nu(\mathrm{CH})$ in the monomeric molecules. On association

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[1] Gabriel, *Ber.*, 1916, **49**, 1115.

[2] Willstätter and Wirth, *Ber.*, 1909, **42**, 1908.

further frequencies appear for the (NH_2) modes, at 3461 and 3174 cm.$^{-1}$ in CCl_4 and also at 3276 cm.$^{-1}$ in the liquid. In similar media the mean value $\frac{1}{2}(\nu_a + \nu_s)$ for the (NH_2) stretching modes is 3464 cm.$^{-1}$ for formamide[3] and 3383 cm.$^{-1}$ for methylamine.[4] In the gaseous state the former is all-planar whilst the methylamine almost certainly has pyramidally directed ($\sim sp^3$) nitrogen valencies. The mean value for thioformamide (3435 cm.$^{-1}$) lies between the above extremes and may, perhaps, be taken to suggest that thioformamide too tends to assume a planar configuration of its nitrogen valencies. The intensity and the appreciable lowering in frequency shown by the $\nu(NH_2)_{\text{associated}}$ modes emphasise the extent and the strength of the hydrogen-bonding in the liquid state.

TABLE 1. *Thioformamide: infrared absorptions (cm $^{-1}$).*

Liquid	CCl_4 soln.	MeCN soln.	Assignment
—	3790(<1)	—	—
—	3685(1)	3657(<1)	—
—	—	3540(1)	—
3481(6)	3495(9)	3406(9)	$\nu_a(NH_2)$
—	3461(sh)	—	—
3320(9)	3374(10)	3312(10)	$\nu_s(NH_2)$
3276(10)	—	3209(9)	$\nu(NH_2)$ associated
3160(10)	3174(3)	3165(7)	
2990(6)	2965(3)	2965(4)	$\nu(CH)$
—	2924(<1)	—	1599 + 1308(?)
2747(3)	2716(1)	2748(1)	1615 + 1123 = 2738 1443 + 1288 = 2731
2455(2)	2459(1)	2476(<1)	1615 + 842 = 2457
2272(1)	—	—	1443 + 842 = 2285 1615 + 673 = 2288
—	1720(1)	1699(2)	2 × 863 = 1726
1657(3)	1658(<1)	—	2 × 842 (liq.) = 1684 3276 − 1615 = 1661
1615(6)	1599(2)	1603(7)	$\delta(NH_2)$
1472(1)	—	1477(1)	842 + 626 = 1468
1457(2)	1457(1)	1457(1)	—
1443(7)	1432(10)	1426(4)	$\nu_a(NCS)$
1324(5)	1308(5)	1315(5)	$\delta(CH)$
1288(3)	1287(5)	1289(7)	$\nu_s(NCS)$
1123(5)	1125(3)	1129(7)	rock (NH_2)
984(5)	942(2)	982(5)	$\gamma(CH)$
824(6)	863(2)	858(8)	$w(NH_2)$
673 (broad)	—	671 (broad)	$t(NH_2)$
626 (broad)	—	—	$\delta(NCS)$

The location of $\nu(CH)$ in thioformamide at 2965 cm.$^{-1}$ compares with values of 2930 cm.$^{-1}$ for formic acid[5] and 2860 cm.$^{-1}$ for formamide (all in CCl_4).

The medium intensity absorption showing the displacements (in cm.$^{-1}$), 1599 (CCl_4) $\longrightarrow$ 1603 (MeCN) $\longrightarrow$ 1615 (liquid), conforms to the location and behaviour expected for the $\delta(NH_2)$ mode.

The remaining well-defined absorptions for the liquid in the rock-salt region (and their relative intensities) are: 1443 (7), 1324 (5), 1288 (3), 1123 (5), 984 (5), 842 (6) cm.$^{-1}$. In vinyl compounds (*i.e.*, $CH_2{=}CHX$) a characteristic band near 990 cm.$^{-1}$ arises from the out-of-plane $\gamma(CH)$ mode: somewhat higher values are found in typical formate derivatives[3, 5, 6] (Table 2), but there is little doubt that the 984 cm.$^{-1}$ feature in thioformamide is the $\gamma(CH)$ absorption. Substituted ethylenes give the range 1300—1400 cm.$^{-1}$ as containing the $\delta(CH)$ mode and further comparison with Table 2 leads to the choice of 1324 cm.$^{-1}$ for this absorption in thioformamide.

It is thus entirely reasonable that the highest and most intense of the frequencies listed above should be taken as $\nu_a(NCS)$, *i.e.*, 1443 cm.$^{-1}$. Randall *et al.*[7] in a set of eighteen

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[3] Evans, *J. Chem. Phys.*, 1954, **22**, 1228.
[4] A. E. Parsons, this Laboratory.
[5] Thomas, *Discuss. Faraday Soc.*, 1950, **9**, 339.
[6] R. L. Jones, Ph.D. Thesis, Univ. Wales, 1955.
[7] Randall, Fowler, Fuson, and Dangl, "Infra-red Determination of Organic Structures," Van Nostrand, New York, 1949.

compounds containing the grouping (R·N=C=S) have found a strong band between 1471 and 1613 cm.$^{-1}$ which they assign to a NCS stretching mode, and more specifically they describe it as ν(C–N). There remains for the fundamental ν_s(NCS) a possible choice between 1288 cm.$^{-1}$ and 1123 cm.$^{-1}$. It is to be expected that this absorption would be appreciably less intense than ν_a(NCS). Some support for the choice of 1288 cm.$^{-1}$ for this mode comes from a comparison with formamide [3] where the corresponding ν_s(NCO) mode is at 1309 cm.$^{-1}$ and where the rocking (NH$_2$) vibration is at 1190 cm.$^{-1}$, which makes its identification with 1123 cm.$^{-1}$ in thioformamide plausible. Whilst it would not be out of the question to reverse the above assignments of ν_s(NCS) and r(NH$_2$) in thioformamide, the choice made seems the more likely one.

TABLE 2. *Deformation* (CH) *wave numbers in formate derivatives.*

	$H{\cdot}CO_2H$	$H{\cdot}CO_2^-$	$H{\cdot}CO{\cdot}NH_2$	$H{\cdot}CO{\cdot}NHMe$
δ(CH)	1374	1365	1391	1389
γ(CH)	1064	1069	1050	1010

There is little guidance as to appropriate values for the w(NH$_2$) and t(NH$_2$) modes, but these could perhaps give rise to the absorptions at 842 and 673 cm.$^{-1}$. By comparison with thiourea [8] where the corresponding vibration is at 629 cm.$^{-1}$, it is not unreasonable to suggest that δ(NCS) may be at 626 cm.$^{-1}$ in thioformamide.

A question of general interest is whether in the spectrum of thioformamide we can recognise a ν(C=S) frequency. Colthup [9] has suggested the range 1300—1400 cm.$^{-1}$ for this vibration but he does not indicate the class of compounds on which the assignment is based. Sheppard [10] on the other hand has examined a number of compounds with this link and has found no clear correlation: Bellamy [11] also studied a limited number of C=S compounds and was unable to identify any bands in the 1300—1400 cm.$^{-1}$ region which could be assigned to ν(C=S). Mecke and Spiesecke [12] have assigned the frequency at 1216 cm.$^{-1}$ in dithioformic acid and that at 1302 cm.$^{-1}$ in thioacetamide to this mode. More recently Mecke, Mecke, and Lüttringhaus [13] have assigned a frequency varying from 1047 to 1208 cm.$^{-1}$ to ν(C=S) in a number of cyclic and open-chain structures. The variation in this frequency at least emphasises the dependence, if not the " mixing ", of this vibration with adjacent bonds; and the shift from 1109 to 1064 cm.$^{-1}$ in the apparent ν(C=S) on deuteration of thiopyrrolidone,[14] having the grouping (–CS·NH–), provides similar evidence.

The difficulty in assigning the description ν(C=S) in many of these cases probably arises from the location of the hypothetical isolated ν(C=S) vibration (say, approximately, 1200 cm.$^{-1}$) near the frequency of the adjacent bond, *i.e.*, ν(C–O) or ν(C–N). Accordingly these frequencies become split into ν_a(XCS) and ν_s(XCS) modes whose separation depends upon the degree of coincidence of the component bond frequencies and upon the interactions (or delocalisation) within the XCS bonds. In such circumstances it becomes very difficult (if not arbitrary) to decide which of the two observed frequencies ν_a(XCS) or ν_s(XCS) has the more ν(C=S) character. This is exemplified in such structures as thiourea where Stewart [8] has placed ν(C=S) at 1413 cm.$^{-1}$: as already indicated, Randall *et al.*[7] preferred to designate the frequency in the 1471—1613 cm.$^{-1}$ range for their NCS compounds as ν(C–N). The obvious uncertainty in these cases serves to emphasise the limitations of the concept of " a characteristic bond frequency."

We conclude that thioformamide is adequately represented by the amide formula but that it is difficult to decide which of the two bonds immediately concerned is principally

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[8] Stewart, *J. Chem. Phys.*, 1957, **25**, 248.
[9] Colthup, *J. Opt. Soc. Amer.*, 1950, **40**, 397.
[10] Sheppard, *Trans. Faraday Soc.*, 1950, **46**, 429.
[11] Bellamy, " The Infra-Red Spectra of Complex Molecules," Methuen, London, 1954.
[12] Mecke and Spiesecke, *Chem. Ber.*, 1956, **89**, 1110.
[13] Mecke, Mecke, and Lüttringhaus, *ibid.*, 1957, **90**, 975.
[14] Mecke and Mecke, *ibid.*, 1956, **89**, 343.

involved in the pseudo-symmetric, and which in the pseudo-antisymmetric stretching mode of the (NCS) grouping.

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