## 799. *An Infrared Study of the Methylhydroxylamines.*

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The five methyl derivatives of hydroxylamine have been prepared, and their infrared spectra recorded between 4000 and 420 cm.$^{-1}$. All were studied in the gaseous state and as liquid or in carbon tetrachloride solution.

From a study of the contours of the vapour absorptions, deductions as to the molecular conformations are possible. The data indicate that the nitrogen valencies are pyramidally inclined and that a skew or *trans*-conformation about the N–O axis is preferred. For the *O*-methyl and *NN*-dimethyl derivatives, and also possibly in *N*-methylhydroxylamine, there is suggestive evidence of two structures' being present in the vapour.

The C–N, N–O, and C–O bond stretching frequencies observed as combined modes for the skeletal vibrations are such as to establish the simple single bonds consonant with the $sp^3$ hybridized states of the C and N atoms. The methyl group frequencies show striking constancy and simplicity in these compounds.

APART from a study of *O*-methylhydroxylamine in the photographic region,[1] no infrared study of the methylhydroxylamines has been reported: neither are there Raman spectra available. These omissions were almost certainly due to the absence of adequately detailed accounts of the preparation and properties of some of the five methyl derivatives of hydroxylamine. Only after much of the present preparative work was complete were we helped by the appearance of satisfactory details for some of them.[2] Our aim was to report the spectra in the region 2—25 μ for the five methylhydroxylamines: to inter-



(I)          (II)
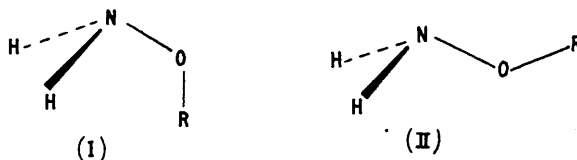
relate and, as far as possible, assign the frequencies to component molecular vibrations: to deduce the probable molecular configurations of these derivatives; and to assess inter-molecular interactions in the liquid or the solution state by comparison of the absorption spectra with those of the vapours. Few simple molecules with adjacent single C–O, C–N, and N–O bonds have been studied by infrared methods, although much attention has

[1] Thompson, *J. Chem. Phys.*, 1939, **7**, 442.
[2] Bissot, Parry, and Campbell, *J. Amer. Chem. Soc.*, 1957, **79**, 796.

been given to the amides and their derivatives in which many complications in relation to molecular vibrational frequencies occur.

The parent compound, hydroxylamine, has been the subject of infrared studies in the vapour and the solid state.[3] A feature of the vapour study was the suggestion of the existence of two isomers, " *cis* " (I; R = H) and " *trans* ", (II; R = H) forms with the possibility of the latter's being, in the vapour, the more stable, although the *X*-ray crystallographic evidence shows the *trans*-conformation in the solid state.[4] Even for the simplest methylhydroxylamine a spectrometer capable of no better resolution than 1 cm.$^{-1}$ (the operating limit for our instrument) will provide only band envelopes for the vapour absorptions. For asymmetric top molecules, such as are all the methylhydroxylamines, Badger and Zumwalt[5] have calculated the contours of band envelopes associated with vibrations in which the dipole-moment change is parallel to the axis of least (A), median (B), or greatest (C) moment of inertia. This they have done in terms of two parameters $s$ and $\rho$ which are simple functions of $I_A$, $I_B$, and $I_C$.

In using Badger and Zumwalt's curves as indications of what the ideal $A$, $B$, and $C$ type vibrational band-contours would be, we have calculated by Hirschfelder's procedure[6] the moments of inertia for alternative plausible configurations of the methylhydroxyl-amine structures. Normal bond lengths and angles have been assumed in these cal-culations: *e.g.*, bond lengths in Å: C–H = 1·09; O–H = 0·96; N–H = 1·01; N–O = 1·46; C–O = 1·43; C–N = 1·47: bond angles, HCH = 109°; HNH = 107°; NOH = 103°; ONH = 105°; CNO = 105°; CNH = 107°, etc. The actual directions of the axes in the assumed structures are readily found by successive trials. In addition to the form of the contours, a check in identification is also possible from the predicted separation of the com-ponent features. Two uncertainties must be faced. First, the direction of the dipole-moment change in a particular vibration can only be approximately fixed for the simplest vibrational forms, *e.g.*, $\nu$(C–O), $\nu$(O–H), $\nu_{sym}$(CH$_3$), $\nu_{sym}$(NH$_2$) $\nu_{as}$(NH$_2$), $d$(O–H), $d$(NH$_2$), etc.; but this



(III)        (IV)        (V)
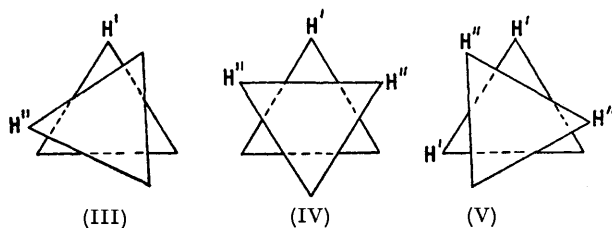
can be done with adequate qualitative correctness, provided the influence of hybridization changes of the " lone pair " electrons on the nitrogen due to orbital-following in the NH$_2$ vibrations, are allowed for. Secondly, only a minority of such vibrations will have dipole changes close to one of the principal axes: the majority will be of a mixed character. Accordingly, only a probability status attends structural deductions based on the identification of the contours.

A significant representation of the conformation around the O–N bond in the hydroxyl-amines is obtained by projecting the structure as seen by looking along the O–N line, if we remember that the " lone-pair " electrons will complete a trigonal pattern about the O and N centres. In this respect it is relevant to recall the skew conformation of the " iso-electronic " molecules hydrogen peroxide (III), hydroxylamine (IV), and hydrazine (V).[7]

[3] Giguère and Lin, *Canad. J. Chem.*, 1952, **30**, 948.
[4] Meyers and Lipscomb, *Acta Cryst.*, 1955, **8**, 583.
[5] Badger and Zumwalt, *J. Chem. Phys.*, 1938, **6**, 712.
[6] J. O. Hirschfelder, *J. Chem. Phys.*, 1940, **8**, 431.
[7] (*a*) See " Tables of Interatomic Distances, etc.," Chem. Soc. Special Publ. No. 11, 1958; (*b*) Penney and Sutherland, *Trans. Faraday Soc.*, 1934, **30**, 898; *J. Chem. Phys.*, 1934, **2**, 492.

For such an angular grouping as $NH_2$ a variety of vibrational modes is involved within a polyatomic structure. For the plane of the equilibrium positions of the atoms the displacements can be represented as in Fig. 1, where, in the probable order of decreasing frequencies we have the antisymmetric $\nu_{as}(NH_2)$ and symmetric $\nu_{sym}(NH_2)$ stretching modes; the in-plane deformation $d(NH_2)$; the twisting, $tw(NH_2)$; the wagging, $w(NH_2)$; and the torsional $to(NH_2)$.

For the $CH_3$ group corresponding modes are often of values *ca.*: $\nu_{as}(CH_3) = 2960$ cm.$^{-1}$; $\nu_{sym}(CH_3) = 2870$ cm.$^{-1}$; $d_{as}(CH_3) = 1450$ cm.$^{-1}$; $d_{sym}(CH_3) = 1380$ cm.$^{-1}$; rocking and wagging of the $H_3$ group in $CH_3$, the former by convention being the motion in the plane

FIG. 1. *Vibrational modes of the $NH_2$ group.*
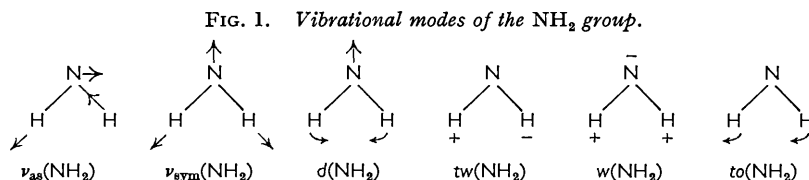


of the skeleton; the wagging motions perpendicular to that plane are within the range 800—1200 cm.$^{-1}$; the torsional mode $to(CH_3)$ *ca.* 300 cm.$^{-1}$. It is the external group vibrational modes (twisting, rocking or wagging, torsional) which are particularly sensitive to the mechanical coupling and bonding between the group and the remainder of the molecule.

*O-Methylhydroxylamine.*—The extreme "*cis*" and "*trans*" conformations for this molecule are represented in Fig. 2, with the positions of the corresponding principal axes and of the so-called "atomic" or better "orbital" moment of the lone-pair electrons: the C-axis is perpendicular to the A,B plane.[7a] These conformations are, respectively, the staggered "*cis*" and eclipsed "*trans*" form: other special orientations around the N–O bond are the eclipsed "*cis*" and staggered "*trans*" forms. For both forms in Fig. 2, in units of $10^{-40}$ g. cm.$^2$, the moments of inertia are $I_A = 31 \pm 2$, $I_B = 92 \pm 2$,

FIG. 2. *Principal axes for the* trans (a) *and* cis (b) *conformations of O-methylhydroxylamine.* (*The* C *axis is at right angles to the plane of the diagram.*)
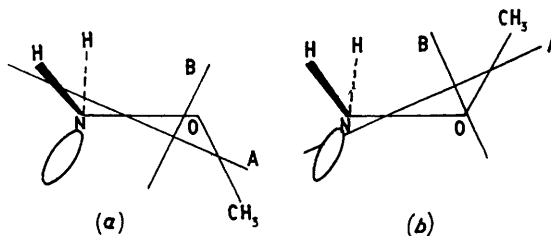


$I_C = 113 \pm 2$. These values predict a separation of the component features in the band contours of *ca.* 15 cm.$^{-1}$, *i.e.*, A and C types will be of total width 30 cm.$^{-1}$; whilst the doublet spacing in B-type absorptions should be near 15 cm.$^{-1}$.

A total of 18 proper modes can be expected for this molecule. Plausible descriptions for 15 of these have already been given, *i.e.*, six modes arising from the $NH_2$ group and nine from the $CH_3$ group, as for the latter the antisymmetric stretching and deformation modes are doubly degenerate. The three remaining vibrations are the "skeletal modes" of the N–O–C group, *i.e.*, $\nu_{as}(NOC)$, $\nu_{sym}(NOC)$, and $d(NOC)$.

The observations are summarized in Table 1. No Raman spectrum is available. Many of the suggested assignments follow from the normal group frequencies and, in particular, there is good correlation with those in "*O*-methylformhydroxamic acid,"[8] $H \cdot CO \cdot NH \cdot O \cdot CH_3$, which is the formyl derivative of *O*-methylhydroxylamine.

[8] Parsons, *J. Mol. Spectroscopy*, 1958, **2**, 566.

The stretching $NH_2$ modes are of particular interest (Fig. 3). In the vapour $\nu_{as}(NH_2)$ appeared as an unsymmetrical contour with a sharp centre at 3414 cm.$^{-1}$ having wings at

TABLE 1. *Infrared absorption frequencies (cm.$^{-1}$) in O-methylhydroxylamine.*

| Liquid | Soln. in CCl$_4$ | Vapour | Assignment | Liquid | Vapour | Assignment |
|---|---|---|---|---|---|---|
| 3539(sh) | | | | 1876vw | | |
| 3377(sh) | | | | | 1600 ⎤ | |
| | | 3429 ⎤ | | | 1592 ⎥ | |
| 3308vs | 3326ms | 3414 ⎬vw | $\nu_{as}(NH_2)$ | 1593s | 1588 ⎬s | $d(NH_2)$ |
| | | 3406 ⎦ | | | 1573 ⎦ | |
| 3294(sh) | | 3289 ⎤ | | 1464s | 1475m | $d_{as}(CH_3)$ |
| | | 3278 ⎥ | | 1438s | 1439m | $d_{sym}(CH_3)$ |
| 3240s | 3244ms | 3269 ⎬vw | $\nu_{sym}(NH_2)$ | 1316ms | 1310vw | $\nu_{sym}(NOC) + d(NOC)$? |
| | | 3256 ⎦ | | 1212m | 1211s | wag.$(CH_3)$ |
| | | 3203 ⎤ | | | 1185 ⎤ | |
| | | 3191 ⎥ | | 1168ms | 1174 ⎬vs | |
| 3157s | | 3181 ⎬vw | $2d(NH_2)$ | | 1152 ⎦ | |
| | | 3168 ⎦ | | 1143ms | 1124m | rock.$(CH_3)$ |
| 2979s | 2982s | 2987s | | | 1015 ⎤ | |
| 2938vs | 2938vs | 2950vs | $\nu_{as}(CH_3)$ | 1012ms | 998 ⎬vs | $\nu_{as}(NOC)$ |
| 2895vs | 2890vs | 2900vs | $2d_{as}(CH_3)$ | | 987 ⎦ | |
| 2811vs | 2812ms | 2817ms | $\nu_{sym}(CH_3)$ | 846s | 858vw | $\nu_{sym}(NOC)$ |
| | | | | 450m | 487w | $d(NOC)$ |

3406 cm.$^{-1}$ and 3429 cm.$^{-1}$. It can only be described as a hybrid form with certainly some $C$-component. Neither is the $\nu_{sym}(NH_2)$ absorption of simple form: it has two central peaks at 3269 and 3278 cm.$^{-1}$ flanked by shoulders at 3256 and 3289 cm.$^{-1}$. This might
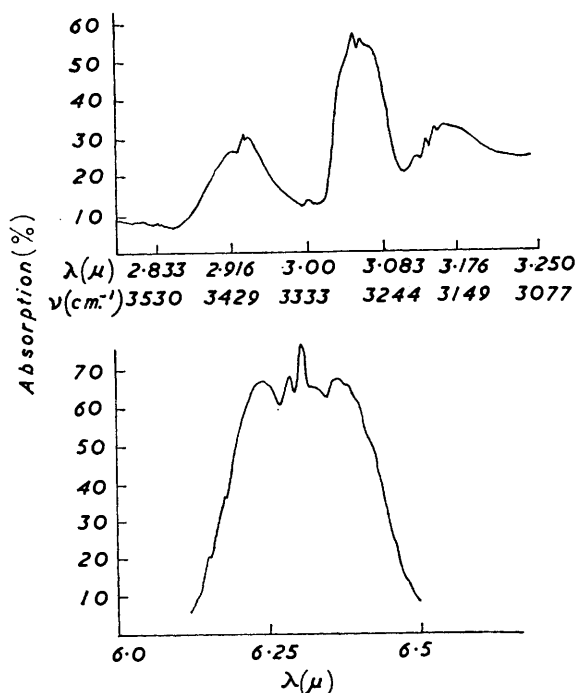


FIG. 3. *The $d(NH_2)$ and $\nu(NH_2)$ bands in O-methylhydroxylamine vapour (traced from the actual records).*

be taken as a $C$- or hybrid $AC$-type absorption but for the second marked central peak at 3278 cm.$^{-1}$. These observations suffice to rule out the " eclipsed *trans* " conformation of Fig. 2, since for that it is expected that $\nu_{as}(NH)_2$ would be a pure $C$-type and $\nu_{sym}(NH_2)$ a pure $B$-type absorption. The alternatives appear to be an " eclipsed *cis* " or a " staggered

*trans* " form. The considerations presuppose the absence of completely free rotation around the N–O bond, but as such freedom is not present in either hydrogen peroxide or hydrazine it is unlikely to be present in *O*-methylhydroxylamine.

The deformation $d(NH_2)$ mode provides further criteria (Fig. 3). Its absorption is certainly that near 1600 cm.$^{-1}$ which, in the vapour, has a distinct *C*-type character with a with a well-defined *Q* branch at 1588 and wings at 1603 and 1573 cm.$^{-1}$. This form leads to the same alternatives as the stretching frequencies but again there is an additional sharp peak, at 1592 cm.$^{-1}$. Being on the high-frequency side of the principal *Q*-branch it is perhaps unlikely that this is a " hot band " associated with the same mode, but it could be a subsidiary absorption (overtone or combination) with an unusually sharp centre. Nevertheless, to rate it no higher, the possibility remains that this second central feature, like that at 3278 cm.$^{-1}$ in $\nu_{sym}(NH_2)$, arises from the presence of two species of molecule having slightly different conformational forms, *e.g.*, that both " eclipsed *cis* " and " staggered *trans* " forms occur. It is significant that a similar state of affairs has been suggested in hydroxylamine itself.

Again, with sufficient vapour in the cell to bring up the $NH_2$ stretching modes, a distinct absorption appears from 3140 to 3200 cm.$^{-1}$ which is too broad to come from a single vibration. The most plausible assignment of this is as an overtone of the relatively intense $d(NH_2)$ absorption, *i.e.*, $2 \times 1588$ cm.$^{-1}$, and the existence of component peaks near 3168, 3181, 3191, and 3203 cm.$^{-1}$ could also be explained by the presence of two molecular species.

The intensities of the $\nu(NH_2)$ absorptions are noteworthy. Although of equal intensity to the $\nu(CH_3)$ modes in the liquid, they are not obvious as vapour absorptions until the cell shows 100% absorption in the $\nu(CH_3)$ region. Contrary to the usual order, but as is found in hydroxylamine itself, the $\nu_{sym}(NH_2)$ is more intense than $\nu_{as}(NH_2)$ in the vapour. An explanation is provided by considering the probable dipole-moment changes during the vibrations, taking particular account of the contributions from the lone-pair electrons— as is also essential in assessing the probable direction of these dipole-moment changes.[9] In carbon tetrachloride solution the sequence of the $NH_2$ intensities has reverted to normal, although they are still less strong than the $\nu(CH_3)$ absorptions, equality with which they attain in the liquid state. For the latter, the $\nu_{as}(NH_2)$ and $\nu_{sym}(NH_2)$ centres are best located at 3308 and 3157 cm.$^{-1}$ respectively, *i.e.*, at values $-106$ and $-112$ cm.$^{-1}$ with respect to the vapour centres. These displacements are a measure of the hydrogen-bridge interaction, most probably (N–H----O) which occurs in the liquid. Adjacent subsidiary maxima (3294 and 3240 cm.$^{-1}$) in the liquid are probably features in the absorption by the hydrogen-bridge structure or (less probably) arise from alternative interactions, *e.g.*, (N----H).

In the region of the $CH_3$ stretching modes four strong centres are found, in order of decreasing intensities in the liquid at 2938, 2895, 2979, and 2811 cm.$^{-1}$, and at closely similar values in carbon tetrachloride. The assignment of the first and the last of these to $\nu_{as}(CH_3)$ and $\nu_{sym}(CH_3)$ is arrived at by consideration of the alternatives and noting the agreement of these values with those in *O*-methylformhydroxamic acid [8] (2941 and 2828 cm.$^{-1}$) and with the findings of Henbest *et al.*[10] for the methyl group in O–CH$_3$ structures.

The absorption at 2895 cm.$^{-1}$ (a similarly strong one is found in $CH_3 \cdot NH_2$ and the methyl halides) can be assigned to the overtone of $d_{as}(CH_3)$, *i.e.*, $2 \times 1464$ cm.$^{-1}$, intensified by its coincidence with the $\nu(CH_3)$ frequency region. This still leaves 2979 cm.$^{-1}$, and it is impossible to assign this frequency (or 2938 cm.$^{-1}$) either as an overtone or as a binary combination tone. It is difficult to resist the suggestion that it is $\nu_{as}(CH_3)$ in a molecular conformation different from that of the 2938 cm.$^{-1}$ absorption: Pozefsky and Coggeshall [11] have recently given for this mode in O–CH$_3$ groupings values of 2960—2990 cm.$^{-1}$. The

[9] Parsons, Ogden, and Orville-Thomas, *J.*, 1958, 1047.
[10] Henbest, Meakins, Nicholls, and Wagland, *J.*, 1957, 1462.
[11] Pozefsky and Coggeshall, *Analyt. Chem.*, 1951, **23**, 1611.

vapour absorption is complicated in the $\nu(CH_3)$ region by the overlapping of bands (Fig. 4): one of the features that can be recognized is the central (Q) branch of a C-type band at 2987 cm.$^{-1}$ which is the 2979 cm.$^{-1}$ absorption of the liquid, and this form agrees with the suggested assignment. The 2985 cm.$^{-1}$ (liquid) absorption becomes a featureless shoulder at 2900 cm.$^{-1}$ in the vapour.

The $d(CH_3)$ bands also overlap in the vapour absorption to such an extent as to make deductions from their contours uncertain, but the centres are at 1475 and 1439 cm.$^{-1}$ compared with 1464 and 1438 cm.$^{-1}$ in the liquid: in O-methylformhydroxamic acid the corresponding values are 1476 (vap), 1468 (liq): 1439 (vap), 1433 (liq). From both its position and its C-type absorption in the vapour centred at 1211 cm.$^{-1}$ there is little doubt that a methyl wagging mode can be recognized—the one out of the (CON) plane. The in-plane rock($CH_3$) is at 1124 cm.$^{-1}$ (vap). In O-methylformhydroxamic acid the same modes appear in the vapour at 1209 and 1124 cm.$^{-1}$.

FIG. 4. *Infrared spectrum of O-methylhydroxylamine vapour at 110° in the region 4000—400 cm.$^{-1}$.*
*(Broken line = increase in amount of vapour.)*
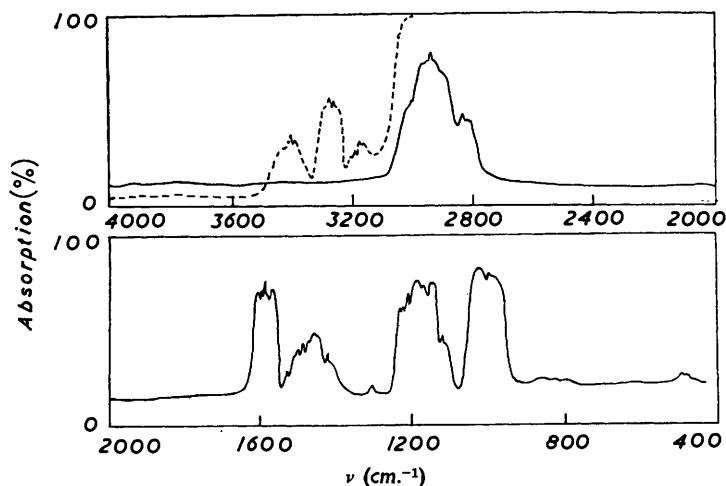


The absorption at 1168 cm.$^{-1}$ (vap), 1174 cm.$^{-1}$ (liq), is an $NH_2$ mode but it is not clear whether it is the twisting or the wagging vibration: the former is thought the more likely. The essentially A-type absorption at 987–998–1015 cm.$^{-1}$ in the vapour is one of the strongest in the spectrum: it is assigned with confidence to $\nu_{as}(NOC)$, which is perhaps very largely the C–O stretching mode. The $\nu_{sym}(NOC)$, or N–O stretching mode, is at 858 cm.$^{-1}$ (vap), 846 cm.$^{-1}$ (liq). In hydroxylamine [3] the same mode appears at 895 cm.$^{-1}$ in the vapour, and calculation on a diatomic model shifts this frequency to 825 cm.$^{-1}$ for the O-methyl derivative.

For the remaining absorption, a weak vapour band at 487 cm.$^{-1}$ (450 cm.$^{-1}$ liq), there are two possible assignments: deformation (NOC) or torsional ($NH_2$). The latter occurs at 430 cm.$^{-1}$ in hydroxylamine and is a plausible choice in the present instance: thus $d(COC)$ in dimethyl ether is at 414 cm.$^{-1}$, and the corresponding mode in methylhydroxylamine might be outside the observed range, as is certainly true of the torsional $CH_3$ mode which we have not found. Another frequency unidentified in the above account is the wagging $NH_2$. This might be relatively weak and lost amongst the overlapping bands at 1100—1250 cm.$^{-1}$ or under the strong $\nu_{as}(NOC)$ at 1000 cm.$^{-1}$.

N-*Methylhydroxylamine.*—In contrast to the O-methylhydroxylamine, which is a volatile liquid (b. p. 48°), this compound is a solid of m. p. 38°, a change which shows the

rôle of hydrogen bridges in the condensed phase. Their influence is also apparent in the differences observed between the liquid and vapour spectra, and as the latter phase shows no signs of such interactions these two sets of observations will suffice for the description of the absorptions.

Fig. 5.
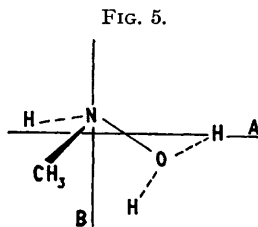
As there is every reason to believe that the nitrogen valencies are pyramidal in hydroxylamine and its *O*-methyl compound, it is reasonable to expect (and observation confirms) that they will be similarly directed in the *N*-methyl compound. This provides configurations of which two extreme versions, the " cis " and the " trans " form, are represented in Fig. 5. Two of the principal axes will be displaced from the CNO plane by only small amounts, and a number of vibrational modes should be essentially of $A$ or $B$ character. A differentiation between the above extreme alternatives should be possible on the basis of the OH group absorptions. The absorptions are summarized in Table 2, and the vapour spectrum is shown in Fig. 6.

There is no doubt about the assignment of $\nu$(OH) to the absorption centred at 3646 cm.$^{-1}$ in the vapour which is of an $A$ or $AC$ type. This suffices to eliminate the " cis " form of Fig. 5, as this would give an essentially $B$-type band, a simple doublet of appreciably smaller separation than the observed features. The amount of $C$-character in $\nu$(OH) is of interest, as it would allow one to assess the approach of that hydrogen atom to the " trans " position in the CNO plane. As judged by comparison both with the Badger–Zumwalt curves and with an essentially pure $A$-type absorption (1032 cm.$^{-1}$ in vapour) there appears to be a significant $C$ component in it. This suggests a skew conformation, and the $d$(OH) vibration, *i.e.*, deformation in the NOH plane, makes this very probable: the absorption has a strong $Q$-branch of distinctly $C$-type (1321 cm.$^{-1}$) which it is difficult to reconcile with the hydrogen in the CNO plane. On the high-frequency side of 1321 cm.$^{-1}$, the pseudo-$P$ branch has such abnormally great breadth and intensity (see Fig. 6) that the presence of another absorption is perhaps the only adequate explanation. This must still arise from the $d$(OH) mode, as the whole of this band disappears completely in the liquid state: thus it is possible that a second (*e.g.*, trans) azimuthal conformation is present with the skew

TABLE 2. *Infrared absorption frequencies* (cm.$^{-1}$) *in N-methylhydroxylamine.*

| Liquid | Vapour | Assignment | Liquid | Vapour | Assignment |
|---|---|---|---|---|---|
| | 3656⎫ | | | 1395vvw | |
| | 3644⎬m | $\nu$(OH) monomer | | 1355⎫(sh) | |
| | 3627⎭ | | | 1333⎪ | |
| 3550—3000vs | | $\nu$(OH) associated | | 1321⎬s | $d$(OH) monomer |
| | 3312w | $\nu$(NH) | | 1306⎭ | |
| 3269s | | $\nu$(NH) | | 1207⎫ | |
| 2978(sh) | 2975s | | 1208m | 1196⎬m | wag.(CH$_3$) |
| 2958s | 2966vs | $\nu_{as}$(CH$_3$) | | 1184⎭ | |
| 2921(sh) | | | | 1140⎫ | |
| 2891s | 2882(sh) | | 1143w | 1126⎬w | rock.(CH$_3$) |
| 2857(sh) | | | | 1121⎭ | |
| 2784m | 2791w | | | 1046⎫ | |
| 1643m | | | 1034vs | 1032⎬ms | $\nu_{as}$(CNO) |
| | 1518s | | | 1018⎭ | |
| | 1480 | | 994m | 956⎫s | $\nu_{sym}$(CNO) |
| 1469m | 1462 | $d_{as}$(CH$_3$) | | 944⎭ | |
| 1440m | 1443 | $d_{sym}$(CH$_3$) | | 841⎫ | |
| | 1419 | | 854s | 828⎬vs | wag.(NH) |
| 1405m | | $d$(OH) associated | | 813⎭ | |
| | | | 457m | | $d$(CNO)? |

form giving a slightly displaced $d$(OH) frequency. It is not unreasonable to envisage this without its being detectable in any other vibrational absorption in the present study, but the suggestion can be only tentative.

There are seven bonds in the eight-atom molecule giving the stretching vibrations conveniently described as $\nu$(OH), $\nu$(NH), $\nu_{as}$(CNO), $\nu_{sym}$(CNO), $\nu_{sym}$(CH$_3$), $\nu_{as}$(CH$_3$), the last

being doubly degenerate. The deformation modes should include vibrations based on $d$(CNO), $d_{sym}$(CH$_3$), $d_{as}$(CH$_3$) (double), rocking (CH$_3$), wagging (CH$_3$), torsional (CH$_3$): in addition there will be two deformations where the H of NH moves in perpendicular planes (*e.g.*, perhaps in and perpendicular to the HNC plane): similarly for the H of OH where the modes can be described as $d$(OH) in the HON plane and torsional or $to$(N–O) in the perpendicular direction.

Considerable hydrogen bonding in the liquid produces a broad absorption in the 3 μ region with a maximum at 3269 cm.$^{-1}$. The latter feature may arise from ν(NH) in the liquid superimposed upon the featureless absorption extending from 3600 cm.$^{-1}$ to below 3000 cm.$^{-1}$, reminiscent of associated OH groups in the alcohols. A weak band seemingly of $B$-type is centred at 3312 cm.$^{-1}$ in the vapour absorptions, and is almost certainly ν(NH) [the mean of the as. and sym. modes in $O$-methylhydroxylamine is 3344 cm.$^{-1}$; and

Fig. 6.   *Infrared spectrum of* N-*methylhydroxylamine vapour at* 48° *in the region* 4000—400 cm.$^{-1}$.
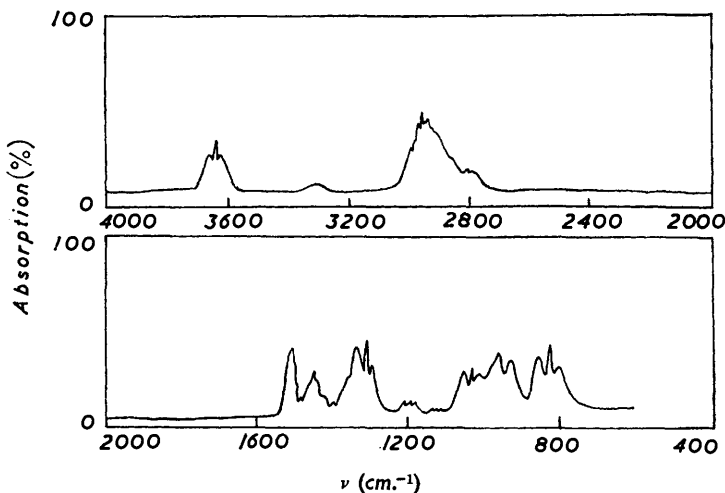


in the $ON$-dimethyl compound, ν(NH) is at 3283 cm.$^{-1}$]. Its $B$-character is to be expected when the changes in the lone-pair orbital are envisaged.

In the liquid spectrum, distinct maxima at 2958, 2891, and 2784 cm.$^{-1}$ are flanked by a number of shoulders. The choice of ν$_{as}$(CH$_3$) as 2958 cm.$^{-1}$ is well supported from related molecules and also 2784 cm.$^{-1}$ for ν$_{sym}$(CH$_3$), as it occurs in the $ON$- and $NN$-di methylhydroxylamines at 2774 and 2776 cm.$^{-1}$, respectively. A feature near 2891 cm$^{-1}$. also occurs in other methylhydroxylamines and appears to be the overtone $2 \times d_{as}$(CH$_3$). In the vapour the overlapping contours provide no clear information.

In the region of the deformation N–H, O–H, and CH$_3$ modes four absorption maxima appear in the liquid spectrum, at 1643, 1469, 1440, and 1405 cm.$^{-1}$. Those at 1469 and 1440 cm.$^{-1}$ are assigned with some confidence to the $d_{as}$(CH$_3$) and $d_{sym}$(CH$_3$) vibrations. In the vapour the overlapping features produce a confused contour but a $Q$-branch is located at 1443 cm.$^{-1}$ and shoulders at 1419 and 1462 cm.$^{-1}$. There is no doubt that the strong vapour absorption centred at 1321 cm.$^{-1}$ and already described is the $d$(OH) mode: in the parent molecule H$_2$N·OH it is at 1357 cm.$^{-1}$; in H$_2$C:N·OH at 1315 cm.$^{-1}$; in (CH$_3$)$_2$C:N·OH at 1340 cm.$^{-1}$; and in (CH$_3$)$_2$N·OH at 1311 cm.$^{-1}$. In the liquid $N$-methyl-hydroxylamine there are no signs of an absorption from 1250 to 1380 cm.$^{-1}$ and it is the 1405 cm.$^{-1}$ absorption in the liquid which is very probably the principal $d$(OH) vibration in that phase. Although there is a small shoulder at 1419 cm.$^{-1}$ in the vapour absorption, this is relatively very much weaker than 1405 cm.$^{-1}$ in the liquid. The shift in frequency

from vapour to liquid ($+84$ cm.$^{-1}$) is characteristic of such deformation modes, especially when the X–H group becomes involved in hydrogen-bonding.

The absorption at 1643 cm.$^{-1}$ is not observed in the vapour. As it occurs in the region of $d$(NH) modes for secondary amines [12] and appears to have its counterpart at 1592 cm.$^{-1}$ in liquid *ON*-dimethylhydroxylamine it is assigned to $d$(NH). In the vapour a very strong absorption does appear at 1518 cm.$^{-1}$ with no definite contour. So striking is its disappearance in the liquid that the possibility was considered that it arose from some decomposition in the vapour, but although minor changes could be observed in the vapour spectrum after more than 3 hr. in the heated (55°) cell, the 1518 cm.$^{-1}$ band was prominent in all the records. It is assigned to $d$(NH) in the vapour and it is noticeable that the liquid has a considerable absorption shoulder from 1500—1600 cm.$^{-1}$ as well as the smaller isolated centre at 1643 cm.$^{-1}$. The latter may well arise from the deformation mode for hydrogen-bonded NH groups, whilst the broad shoulder is the same mode for the unbonded NH groups in the liquid. On this basis both $d$(OH) and $d$(NH) show greater integrated intensities in the vapour than in the liquid state, a reversal of the intensity changes in $\nu$(OH) and $\nu$(NH) between the two phases. This pattern of behaviour could well be correlated with the propositions (i) that the X–H bonds acquire greater polar character on being extended in the hydrogen bridge (and hence the stretching modes become more intense and displaced to lower frequencies); (ii) that the hybridization changes in the lone-pair electrons are far greater in the deformation than in the stretching modes; (iii) that such changes are the principal components in the dipole elements involved in the deformation intensities; and (iv) that they are reduced by the smaller amplitudes and higher frequencies of the deformation modes in the hydrogen-bridge systems.

FIG. 7.



" cis " " trans "
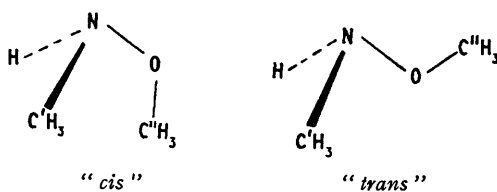
The rocking CH$_3$ frequencies are assigned to 1196 cm.$^{-1}$ (vap) $\longrightarrow$ 1208 cm.$^{-1}$ (liq); 1126 cm.$^{-1}$ (vap) $\longrightarrow$ 1143 cm.$^{-1}$ (liq), the former probably being that out of the CNO plane although it appears to lack the *C*-character expected of such a mode. The C–N and N–O bonds will have stretching frequencies of the same order and so will combine to give $\nu_{as}$(CNO) and $\nu_{sym}$(CNO) of the triatomic system. These are recognised with some confidence from the distinctively *A*- and *B*-type absorptions in the vapour centred at 1032 cm.$^{-1}$ and 950 cm.$^{-1}$, respectively (cf. 998 cm.$^{-1}$ and 858 cm.$^{-1}$, respectively, in H$_2$N·O·CH$_3$). The second deformation mode of NH, perhaps essentially in the HNO plane and describable as a wagging mode, is identified with the *A*- or *AC*-type vapour absorption at 828 cm.$^{-1}$ which, as expected, increases in frequency (to 854 cm.$^{-1}$) in the liquid. The only other absorption found was for the liquid at 457 cm.$^{-1}$. Two of the remaining three proper modes might occur here: the skeletal deformation $d$(CNO) or the OH torsional or $to$(NO) mode. No good grounds for a choice between these can be advanced although it is reasonably certain that $d$(CNO) will occur near this frequency; the torsional CH$_3$ mode is again outside the potassium bromide prism range.

*ON-Dimethylhydroxylamine.*—This compound, b. p. 42°, was examined as a liquid and vapour. The absence of a hydroxyl group reduces the hydrogen-bonding interactions in the liquid to an extent such that the only obvious change in the absorptions on change of phase is a shift of 50 cm.$^{-1}$ in the $\nu$(NH) centre and the breadth of its absorption in the liquid.

[12] Bellamy, " Infra-Red Spectra of Complex Molecules," Methuen, London, 1954.

Courtauld models show that the *cis*-conformation of this dimethyl derivative (cf. Fig. 7) would show appreciable congestion of the methyl groups, and something more nearly approaching the *trans*-form is probable.

TABLE 3.    *Infrared absorption frequencies* (cm.$^{-1}$) *in* ON-*dimethylhydroxylamine.*

| Liquid | Vapour | Assignment | Liquid | Vapour | Assignment |
|---|---|---|---|---|---|
| 3234m | 3283vw | $\nu$(NH) | 1153w | 1156w | rock.$(CH_3)$–O |
|  | 3194vw |  | 1133w | 1145w | rock.$(CH_3)$–N |
|  | 3135vw | 2$d$(NH) |  | 1075⎫ |  |
| 2977ms | 2991(sh) | $\nu_{as}(CH_3)$–N | 1057vs | 1064⎬vs | out-of-phase |
| 2939s | 2954s | $\nu_{as}(CH_3)$–O |  | 1059⎭ | $\nu$(CN) + $\nu$(CO) |
| 2886m | 2899s | 2$d_{as}(CH_3)$ |  | 1032⎫ |  |
| 2860(sh) |  |  | 1019m | 1022⎬s | in-phase |
| 2809m | 2816s | $\nu_{sym}(CH_3)$–O |  | 1014⎭ | $\nu$(CN) + $\nu$(CO) |
| 2775m | 2784(sh) | $\nu_{sym}(CH_3)$–N |  | 940⎫ |  |
|  | 1610⎫ |  | 928s | 933⎬vs | $\nu$(NO) |
| 1592 | 1600⎬w | $d$(NH) |  | 926⎭ |  |
|  | 1590⎭ |  |  | 813⎫ |  |
| 1476(sh) | ⎫ |  | 799ms | 803⎬m | wag.(NH) |
| 1460m | 1473ms⎬ | $d_{as}(CH_3)$ |  | 793⎭ |  |
| 1441m | 1434ms | $d_{sym}(CH_3)$ | 515(sh) |  |  |
| 1219m | 1215⎫ | wag.$(CH_3)$–O | 475 | 478⎫ | $d$(CNOC)? |
|  | 1202⎭s |  |  | 457⎭m |  |
| 1184m |  | wag.$(CH_3)$–N |  |  |  |

To the total of 27 vibrational modes, each methyl group will contribute nine. As the likelihood of coupling between the vibrations within these groups is small, any distinction between the nine pairs of frequencies will depend upon whether $(CH_3)$–O and $(CH_3)$–N

FIG. 8.    *Infrared spectrum of* ON-*dimethylhydroxylamine liquid in the region* 4000—400 cm.$^{-1}$.
( . . . . = *thicker film.*)
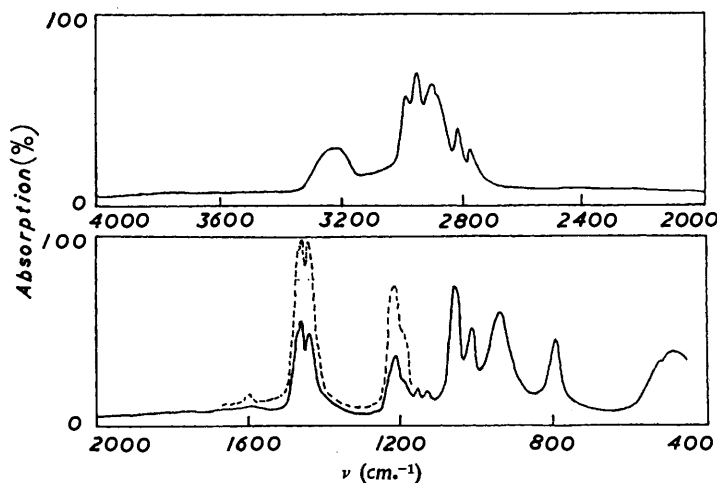


vibrations differ sufficiently.    The NH group will contribute one stretching and two bending modes.    Three of the remaining six modes will be formed from combinations of the bond stretchings, $\nu$(C'N), $\nu$(NO), $\nu$(C''O); two will be angular deformations $d$(C''ON), $d$(C'NO), and finally, a twisting of the skeleton can be described as torsion of the N–O bond.    Any attempt to assign a configuration to this molecule on the basis of the band contours is hindered by the fact that it is difficult to attain any certainty as to the form of the skeletal vibrations, because of coupling between the closely similar bond-stretching frequencies.

The observations are summarized in Table 3 and the liquid spectrum is shown in Fig. 8. Most of the assignments are unexceptional.    The extreme weakness of $\nu$(NH) in the

vapour may be noted; it was recorded in an 8 cm. cell at almost atmospheric pressure and was then accompanied by combination tones at 3194 and 3135 cm.$^{-1}$, one of them (3135 cm.$^{-1}$) probably an overtone of the weakly-absorbing deformation mode $d$(NH) at 1600 cm.$^{-1}$. The $A$-type contour for the latter is one feature providing unequivocal support for a " *trans* "-form of the molecular skeleton.

Whilst a multiplicity of centres both in the liquid- and in the vapour-phase absorptions can be sensibly correlated with the $\nu$(CH$_3$)–N and $\nu$(CH$_3$)–O frequencies shown by related molecules in the 3000 cm.$^{-1}$ region, the deformation CH$_3$ modes show scarcely any signs of differentiation beyond a shoulder at 1476 cm.$^{-1}$ on the main $d_{as}$(CH$_3$) centre at 1460 cm.$^{-1}$ (liquid). A group of four absorptions between 1130 and 1220 cm.$^{-1}$ can be plausibly ascribed, two each to the rocking of the (CH$_3$)–N and (CH$_3$)–O modes. A further group of strong absorptions between 800 and 1060 cm.$^{-1}$ must contain the three skeletal stretching modes. By comparison with non-planar X$_2$Y$_2$ molecules it seems probable that two of these modes may be essentially in-phase and out-of-phase combinations of $\nu$(C'N) and $\nu$(C''O), whilst a third will be a largely symmetrical stretching which could be designated $\nu$(NO). These descriptions can be plausibly given the 1019, 1057, and 928 cm.$^{-1}$ liquid absorptions. The frequencies are in good agreement with expectations from the component bond vibrations in related molecules: thus $\nu$(NO) is at 956 cm.$^{-1}$ in CH$_3$·NH·OH and at 858 cm.$^{-1}$ in H$_2$N·O·CH$_3$. The remaining absorption in the NaCl region at 799 cm.$^{-1}$ in the liquid, 803 cm.$^{-1}$ in the vapour, is assigned to the wagging NH mode: the only surprising feature is its much greater intensity than the other NH modes.

In the KBr region the liquid shows a broad absorption around 475 cm.$^{-1}$, with a shoulder at 515 cm.$^{-1}$; corresponding features appear, somewhat displaced in frequencies in the vapour. Probably two absorptions are present and it is reasonable to claim, although impossible to establish, that they are both fundamentals: they could be the " in-plane " angular distortion modes of the (CNOC) skeleton. A maximum of 24 out of the 27 fundamentals would thus be accounted for.

NN-*Dimethylhydroxylamine.*—Accepting a pyramidal configuration for the nitrogen valencies, we see that this molecule will be a close approximation to a symmetrical top, the groups attached to the nitrogen atom being CH$_3$, CH$_3$, and OH. The one feature open to uncertainty is the orientation of the OH group, and only the $\nu$(OH) and $d$(OH) modes will be influenced by that. The extreme positions shown in Fig. 9 are " *cis* " and " *trans* "



FIG. 9.
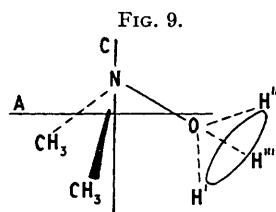
in the plane bisecting the (CNC) angle, which is also the plane of the $A$ axis. As it is reasonable to assume for the polar OH group that in $\nu$(OH) the dipole-moment change will be essentially in the O–H direction, this will be largely of $C$, $AC$, or $B$ character according as the hydrogen is *cis* (H'), *trans* (H''), or skew (H'''). The deformation mode $d$(OH), with the hydrogen moving perpendicularly to the O–H line in the NOH plane, will in all cases produce a dipole change closely parallel to the N–O line and so of $AC$ character in absorption.

The $\nu$(OH) absorption in the vapour (Fig. 10) reproduces on one side a $C$-type contour, but this is clearly overlaid on the low-frequency side by some further absorption. One suggestion to account for this is the simultaneous presence of two different OH conformations, although it is difficult to specify which. This proposal is strongly supported by the appearance of the $d$(OH) absorption at 1311 cm.$^{-1}$ in the vapour (Fig. 10). This shows two small central $Q$-branches separated by only 4 cm.$^{-1}$ and each of which might have originated in an $AC$-type absorption. The total width of the strong shoulders of this absorption (1290—1336 cm.$^{-1}$) emphasizes the presence of two overlapping features of essentially similar structure. As only the OH modes show this doubling of $Q$-branches, it is reasonable to associate the features with that group, *i.e.*, with the presence of two angular configurations for the HO group, rather than with the appearance of " hot " bands superimposed on the normal absorptions.

The NN-dimethylhydroxylamine, like the ON-dimethyl compound, will have 18 fundamental modes associated with the two methyl groups; the hydroxyl group will have its stretching and two bending modes; and the $C_2NO$ skeleton will provide the remaining six. Three of the latter will be stretching modes, and as they will have as their origin three similar bond frequencies each involving the central nitrogen, appreciable coupling between them may be given vibrational forms corresponding to those of the pyramidal molecules ($NX_3$, etc.).

The observations on the liquid and vapour are briefly summarized in Table 4 and the vapour spectrum is shown in Fig. 11. The hydrogen bonding produces an even larger influence on $\nu$(OH) in the liquid than occurs in N-methylhydroxylamine. In the dimethyl compound the shift from the vapour centre in ca. 410 cm.$^{-1}$. The strength of the hydrogen bond in these instances is shown by both hydroxyl compounds' having an associated $\nu$(OH)

FIG. 10. *The $\nu$(OH) and d(OH) bands in the vapour spectrum of* NN-*dimethylhydroxylamine (traced from the actual records).*
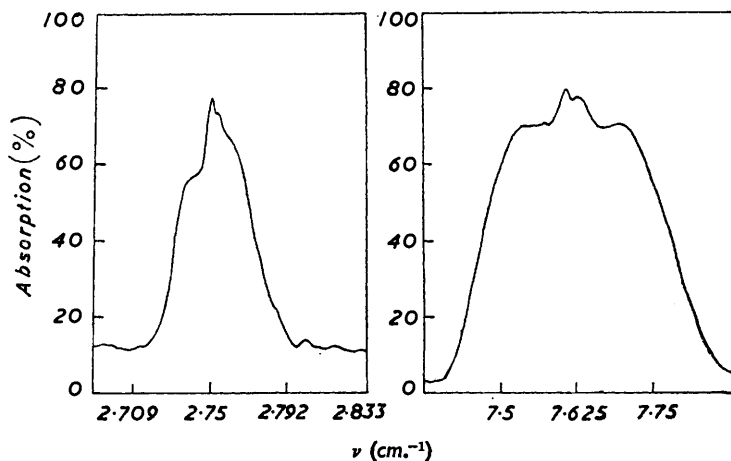


feature in the vapour state which disappears on rise of temperature. In the N-methyl compound it is at 3312 cm.$^{-1}$, or 344 cm.$^{-1}$ from the monomer centre; in the dimethyl compound it is at 3271 cm.$^{-1}$, i.e., 365 cm.$^{-1}$ from the monomer centre.

TABLE 4. *Infrared absorption frequencies (cm.$^{-1}$) in* NN-*dimethylhydroxylamine.*

| Liquid | Vapour | Assignment | Liquid | Vapour | Assignment |
|---|---|---|---|---|---|
| | 3651 ⎫ | | | 1210 ⎫ | |
| | 3636 ⎬ ms | $\nu$(OH) monomer | 1204m | 1199 ⎬ ms | wag.(CH$_3$) |
| | 3631 ⎪ | | | 1179 ⎭ | |
| | 3621 ⎭ | | 1170 ⎫ | | |
| 3600—3000 | 3400—3200 | $\nu$(OH) associated | 1161(sh) ⎬ | 1154m | rock.(CH$_3$) |
| 2985(sh) | 2966vs | $\nu_{as}$(CH$_3$) | 1090 | 1089vw | |
| 2946vs | | ,, | 1054w | 1069vw | |
| 2865(sh) | 2867vs | ,, | 999m | 1000m | skeletal stretch- |
| 2857vs | | ,, | | | ing: $\sim\nu_{as}$(CNC) |
| 2821(sh) | 2823(sh) | ,, | | 962 ⎫ | |
| 2774s | 2778s | $\nu_{sym}$(CH$_3$) | 956ms | 950 ⎬ ms | skeletal stretch- |
| | 1710vw | | | 934 ⎭ | ing: $\sim\nu$(NO) |
| 1655m | | | | 803 ⎫ | |
| | 1586vw | | | 793 ⎬ vs | skeletal stretch- |
| 1472s | 1477s | $d_{as}$(CH$_3$) | 807s | 776 ⎭ | ing: $\sim\nu_{sym}$(CNC) |
| 1439s | 1449s | $d_{sym}$(CH$_3$) | | | skeletal deform- |
| 1419(sh) | | | 501m | | ation |
| | 1323 ⎫ | | | | |
| | 1314 ⎪ | | | | |
| 1313vw | 1310 ⎬ vs | d(OH) | | | |
| | 1300 ⎭ | | | | |

The stretching and deformation modes within the $CH_3$ groups are assigned in good conformity with the frequencies found from other molecules. Between the extreme centres (2966 and 2778 cm.$^{-1}$) for the $\nu(CH_3)$ frequencies, which are recognisably $(CH_3)$–N values, a number of peaks appear which may well be various combinations of these modes between the two methyl groups present. The 1439, 1472 cm.$^{-1}$ features in the liquid, which are $d(CH_3)$ centres, form peaks on an absorption whose breadth indicates the

Fig. 11. *Infrared spectrum of* NN-*dimethylhydroxylamine vapour at* 98° *in the region* 4000—400 cm.$^{-1}$.
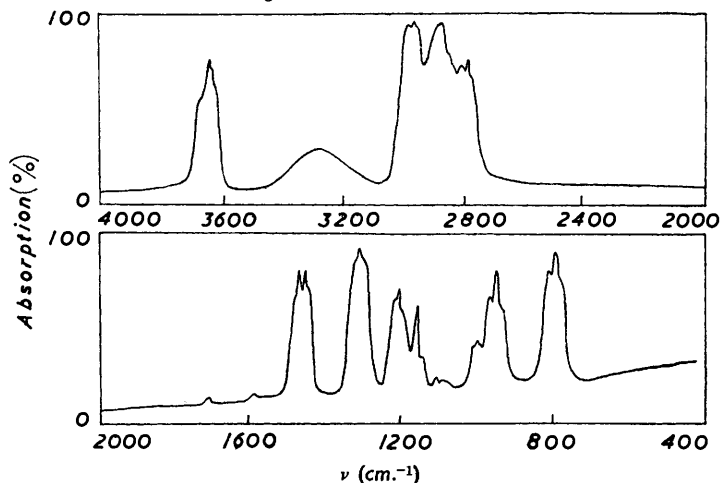


presence of more than two frequencies. It could be that the breadth arises from the coupling of the $d(CH_3)$ modes of the two methyl groups, but this seems unlikely in view of the normal width of the same two overlapping absorptions in the vapour. Accordingly, as the very strong $d(OH)$ absorption in the vapour at 1312 cm.$^{-1}$ almost completely disappears in the liquid (a small peak appears at 1313 cm.$^{-1}$ which could be a combination tone, *e.g.*, 807 + 501 cm.$^{-1}$), it is natural to suggest that $d(OH)$ in the liquid is under the $d(CH_3)$ absorptions and may have its centre in the shoulder seen at 1419 cm.$^{-1}$. However, an alternative is that the absorption at 1655 cm.$^{-1}$, which is very obvious in the liquid but has no counterpart in the vapour, is the $d(OH)$ in the condensed phase. This would mean an exceptionally large displacement from the vapour (1655—1312 cm.$^{-1}$), but the intensity of the 1655 cm.$^{-1}$ feature in the liquid is difficult to account for unless it in some way involves the OH group. It could perhaps be a combination of $d(OH)$ in the liquid with a low deformation mode (*ca.* 250 cm.$^{-1}$), *e.g.*, the torsional or other vibration of the associated OH group.

The vapour absorption at 1199 cm.$^{-1}$ (1204 cm.$^{-1}$, liq.) is somewhat stronger than one at 1154 cm.$^{-1}$ (1170 cm.$^{-1}$, liq.): although the former has a hybrid and somewhat irregular contour (partly, it seems, from overlap with the 1154 cm.$^{-1}$ band), the latter is of a distinctly C-character. These are two methyl modes, the wagging and the rocking vibration: in dimethylcyanamide, where the $(CH_3)_2N$ grouping also occurs, the absorptions are at 1205 and 1146 cm.$^{-1}$. Unless there is no coupling between the methyl groups, these two modes should each be double. No obvious signs of such coupling between the internal modes of the $CH_3$ groups are found in the spectrum, but this by no means precludes its occurrence for the external modes. At 1089 and 1069 cm.$^{-1}$ in the vapour (1090 and 1054 cm.$^{-1}$ in the liquid) there are weak absorptions which could well be the other members of the pairs of wagging and rocking modes. The further specification of these absorptions is speculative.

In the region of the skeletal stretching frequencies three absorptions are found at 999,

956, and 801 cm.$^{-1}$ in the liquid and at closely similar values in the vapour where their contours are $A$ (or $AB$), $C$, and $C$. An appropriate pyramidal molecule for comparison with the dimethylhydroxylamine is trimethylamine.[13] In the latter the symmetric C–N stretching frequency is at 825 cm.$^{-1}$, the doubly degenerate antisymmetric stretching is at 1036 cm.$^{-1}$. Accordingly, 801 cm.$^{-1}$ in dimethylhydroxylamine corresponds to the former, and the 999 and 956 cm.$^{-1}$ features are antisymmetric stretching modes. An alternative description is to take the 999 and 801 cm.$^{-1}$ frequencies as $\nu_{as}$(CNC) and $\nu_{sym}$(CNC) [cf. 1070 and 780 cm.$^{-1}$ in (CH$_3$)$_2$N·CN], with the 956 cm.$^{-1}$ absorption as essentially $\nu$(NO) [cf. what has been described as $\nu$(NO) in NH$_2$·O·CH$_3$ at 858 cm.$^{-1}$; in CH$_3$·NH·OH at 950 cm.$^{-1}$; in CH$_3$·NH·O·CH$_3$ at 933 cm.$^{-1}$].

The one strong absorption in the KBr region is at 501 cm.$^{-1}$ (liq.). It is probably a bending of the skeleton [cf. similar vibrations in (CH$_3$)$_3$N at 423 cm.$^{-1}$ (Raman) and in (CH$_3$)$_2$N·CN at 630 cm.$^{-1}$]. Other fundamentals are either too weak to be observed or occur outside the observed frequency range.

*Trimethylhydroxylamine.*—The volatility of this compound (b. p. 30°) meant that the liquid spectrum could not readily be recorded at room temperature and so the observations were for a 0·73M-solution in carbon tetrachloride (2000—900 cm.$^{-1}$) and for the vapour. Of the 36 normal modes, 27 will arise from methyl-group motions; the remaining nine will consist of four bond-stretching modes and five angular deformations of the (C$_2$NOC) skeleton. The uncertainty in the coupling of the various group frequencies makes the interpretation of band contours in terms of molecular conformation impossible.

In the 3 $\mu$ region, no less than seven distinct absorptions are found in the carbon tetrachloride solution of trimethylhydroxylamine. These can be designated as in Table 5 by reference to the other molecules in this series. In the vapour (Fig. 12), the rotational wings acquired by the vibrational stretching frequencies cause much overlapping of the component absorptions. There is much less suggestion of differentiation between the CH$_3$ groups in the deformation modes. Two clearly defined centres in the solution spectrum at 1470 and 1446 cm.$^{-1}$ correspond to the two peaks at 1477 and 1451 cm.$^{-1}$ which are the only features distinguishable in the vapour. There is also marked simplicity in the form of the rocking CH$_3$ frequencies near 1200 cm.$^{-1}$.

Four bands at 1060, 1005, 941, and 775 cm.$^{-1}$ have their counterparts at 1052, 991, and 934 cm.$^{-1}$ in carbon tetrachloride, which itself absorbs strongly below 850 cm.$^{-1}$. Consideration of the alternatives, and more particularly of the intensities, suggests that these

TABLE 5. *Infrared absorption frequencies* (cm.$^{-1}$) *in trimethylhydroxylamine.*

| Soln. in CCl$_4$ | Vapour | Assignment | Soln. in CCl$_4$ | Vapour | Assignment |
|---|---|---|---|---|---|
| | 3000 ⎫ | | 1198(sh) | | wag.(CH$_3$)–N |
| 2987s | 2989 ⎬ s | $\nu_{as}$(CH$_3$)–N | 1154m | 1155m | rock.(CH$_3$)–N |
| | 2966 ⎭ | | 1086m | | rock.(CH$_3$)–O? |
| 2957s | 2953s | $\nu_{as}$(CH$_3$)–O | | 1070 ⎫ | |
| 2939 | | | 1052vs | 1060 ⎬ vs | skeletal stretching: out-of-phase |
| 2894s | 2893s | 2$d_{as}$(CH$_3$)? | | 1054 ⎭ | [$\nu_{as}$(CNC) + $\nu_{as}$(CON)]? |
| 2864s | 2874s | 2$d_{sym}$(CH$_3$)? | 991m | 1005w | skeletal stretching: in-phase |
| 2811m | 2819ms | $\nu_{sym}$(CH$_3$)–O | | | [$\nu_{as}$(CNC) + $\nu_{as}$(CON)]? |
| 2777(sh) ⎫ | 2787 ⎫ m | $\nu_{sym}$(CH$_3$)–N | 934ms | 941ms | skeletal stretching: [$\nu_{sym}$(CNC)]? |
| 2769m ⎭ | 2776 ⎭ | | | 782 ⎫ | |
| 1470ms | 1477ms | $d_{as}$(CH$_3$) | | 775 ⎬ ms | skeletal stretching: [$\nu_{sym}$(CON)]? |
| 1447ms | 1451ms | $d_{sym}$(CH$_3$) | | 766 ⎭ | |
| 1211m | 1214m | wag.(CH$_3$)–O | | 532vw | skeletal deformation |

stretching frequencies can be described as follows. The (C′NC″) group contributes a $\nu_{as}$(C′NC″) and $\nu_{sym}$(C′NC″) mode, and the adjacent (NOC″) group has two similar modes. The two-component three-particle antisymmetric modes give rise to frequencies which

[13] Navech, Mattis, and Noël-Mathis, *Compt. rend.*, 1957, **244**, 1913; Edsall, *J. Chem. Phys.*, 1937, **5**, 225.

are close together, and one molecular mode will consist of their vibrations being in-phase, another of their out-of-phase motions. These can plausibly be assigned the 1059 and 1003 cm.$^{-1}$ frequencies. The remaining bands are due to the two three-particle " symmetric " vibrations; there is possibly only slight coupling between these frequencies, as 775 cm.$^{-1}$ is close to $\nu_{sym}(C'NC'')$ in dimethylcyanamide (767 cm.$^{-1}$) and in *NN*-dimethylhydroxyl-amine (776 cm.$^{-1}$).

The one absorption in the KBr region, at 522 cm.$^{-1}$, matches the similar feature in *NN*-dimethylhydroxylamine: it is quite possibly $d(C'NC'')$ in both these cases.

*General Conclusions.*—The accumulated data suggest a picture of the hydroxylamines as a group of molecules conforming to normal single-bond conditions. Both the observed contours and the N–H frequencies (where they occur) confirm a pyramidal ($sp^3$) conform-ation of the nitrogen valencies, and the bond frequencies emphasize the essentially single-bond character of the molecules. This condition predisposes the structures to free rotation around the N–O bond, and a feature of particular interest is the preferred orientation assumed in these circumstances.

FIG. 12.   *Infrared spectrum of trimethylhydroxylamine vapour at 25° in the region 4000—400 cm.$^{-1}$.*
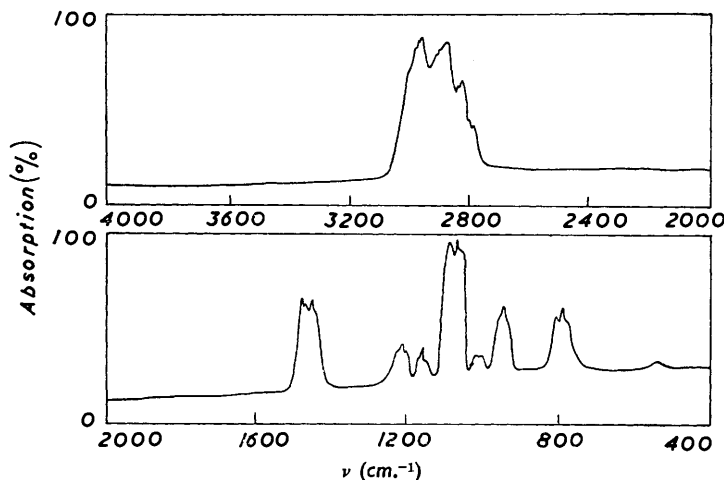


Essentially skew structures are found in the parent hydroxylamine and the related hydrogen peroxide and hydrazine, and the evidence is fairly conclusive that two conform-ations are present in the vapour state of hydroxylamine itself. A similar condition is very likely for a number of the methylhydroxylamines. Suggestive evidence for two structures' being present in the vapour is shown by the doubling of particular absorption

TABLE 6.   *Simplified stretching frequencies (vapour values) in the methylhydroxyl-amines (cm.$^{-1}$).*

| Hydroxylamine | | $\nu$(C–O) | $\nu$(C–N) | $\nu$(N–O) |
|---|---|---|---|---|
| O-Methyl | ........................ | 998 | | 858 |
| N-Methyl | ........................ | | 1032 | 950 |
| ON-Dimethyl | ........................ | 1062 | 1022 | 933 |
| NN-Dimethyl | ........................ | | 900 * | 950 |
| Trimethyl | ........................ | 1005 | 917 | 941 |

\* Mean of proposed $\nu_{as}$(CNC) and $\nu_{sym}$(CNC) values.

centres in the O-methyl and the *NN*-dimethyl compound and, with less weight, also in the *N*-methylhydroxylamine. In these cases there is strong probability that one (and maybe the principal) form is a " staggered *trans* " or skew conformation about the N–O bond.

There is also spectroscopic evidence for a *trans*-form of the skeleton in the *ON*-dimethyl compound, and normal van der Waals radii give the *trans*-orientation distinct preference for the trimethylhydroxylamine. Both general considerations and the existence of

TABLE 7. *Methyl-group frequencies in the substituted hydroxylamines.*

| | *O*-Methyl | *N*-Methyl | *ON*-Dimethyl | *NN*-Dimethyl | Trimethyl |
|---|---|---|---|---|---|
| $\nu_{as}(CH_3)$–O ........................... | 2938 | — | 2939 | — | 2939 |
| $\nu_{sym}(CH_3)$–O ........................ | 2811 | — | 2809 | — | 2811 |
| $\nu_{as}(CH_3)$–N ........................... | — | 2958 | 2977 | $\begin{cases}2985\\2946\end{cases}$ | $\begin{cases}2987\\2957\end{cases}$ |
| $\nu_{sym}(CH_3)$–N ...................... | — | 2784 | 2775 | 2774 | $\begin{cases}2777\\2769\end{cases}$ |
| $d_{as}(CH_3)$ ............................ | 1464 | 1469 | $\begin{cases}1476\\1460\end{cases}$ | 1472 | 1470 |
| $d_{sym}(CH_3)$............................ | 1438 | 1440 | 1441 | 1439 | 1447 |
| Wagging $(CH_3)$ out-of-plane ... | 1212 | 1208 | $\begin{cases}1219\\1184\end{cases}$ | 1204 | $\begin{cases}1211\\1198\end{cases}$ |
| Rocking $(CH_3)$ in-plane ......... | 1143 | 1143 | $\begin{cases}1153\\1133\end{cases}$ | $\begin{cases}1170\\1161\end{cases}$ | $\begin{cases}1154\\1086(?)\end{cases}$ |

alternative forms indicate that only small energy differences arise on rotation of these structures about the N–O bond.

Even the simplest of these compounds has a three-atom (NOC or CNO) framework, which means that coupling between its component vibrations will occur in the observed frequencies. It is significant that, despite this, no skeletal stretching mode has a frequency above 1070 cm.$^{-1}$, a limitation which shows the C–O, C–N, and N–O bonds concerned to be essentially single. To illustrate this aspect of the results one can make the drastic simplification of assuming that in (NOC) the higher stretching frequency is $\nu$(C–O), and that in (CNO) it will be $\nu$(C–N), then the frequencies are as in Table 6. Apart from establishing values close to those normal for such single bonds, the simplification of Table 6 shows the limitations of " characteristic bond frequencies." In all these instances the vibrations are not only of similar frequencies but are linked through common atoms so that isolated modes cannot be expected.

It is well known that the X–H modes are amongst the most constant of characteristic frequencies owing to the isolation of the motion of the hydrogen. This is borne out by the frequencies associated with the $CH_3$ group. The frequencies in Table 7 show a remarkable consistency. The small shifts in the stretching frequencies between $(CH_3)$–O and $(CH_3)$–N are, in fact, merely an expression of the slightly greater splitting between the antisymmetric and symmetric modes when the methyl group is attached to nitrogen. The arithmetic means of the two frequencies are: for the $(CH_3)$–O groups 2875, 2874, 2875 cm.$^{-1}$; for the $(CH_3)$–N groups, 2871, 2876, 2870, 2873 cm.$^{-1}$. Thus no difference in the C–H bonds is observed on this criterion.

It is perhaps even more surprising that the $d(CH_3)$ modes show such constancy, since, as judged from the methyl halides, these modes (and especially $d_{sym}$) are much more sensitive to changes in the attachment of the methyl radical. However, there are indications that it is the mass factor associated with X in $CH_3$–X which is significant in this respect.[14] Even so, it is remarkable that such little splitting of these modes occurs when two or more groups are present—so little that the vapour bands frequently appear as single well-defined modes. This simplicity is further emphasized by the similar behaviour of the $CH_3$ wagging and rocking modes.

Thus the general conclusion from this study of the methylhydroxylamines is that they show the simple structural relations expected from their " classical " single-bond formulæ. The adjacent C–N, C–O, and N–O bonds show no signs of those interactions so characteristic of amide structures, a condition which arises from the $sp^2$ hybridization of both carbon

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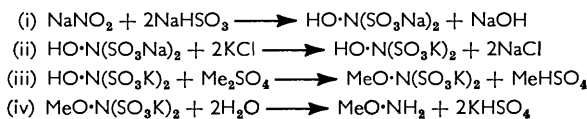[14] Davies and Hallam, *Trans. Faraday Soc.*, 1951, **47**, 1170.

and nitrogen atoms in those compounds but is precluded in the hydroxylamines by the essentially $sp^3$ valency states of the atoms.

<div align="center">EXPERIMENTAL</div>

The spectra were obtained by using the Grubb-Parsons G.S.2 double-beam grating spectrometer from 4000 to 650 cm.$^{-1}$, and the S.3 single-beam with KBr prism from 700 to 420 cm.$^{-1}$. The calibration of the former was checked by using Plyler's values for polystyrene film, and the KBr range from well-established frequencies [15] in $CO_2$, $CCl_4$, PhMe, and $CHBr_3$. Conventional liquid cells and an 8 cm. gas cell which could be heated uniformly were available.

*O*-Methylhydroxylamine was prepared by the sequence: [16]

(i) $NaNO_2 + 2NaHSO_3 \longrightarrow HO \cdot N(SO_3Na)_2 + NaOH$

(ii) $HO \cdot N(SO_3Na)_2 + 2KCl \longrightarrow HO \cdot N(SO_3K)_2 + 2NaCl$

(iii) $HO \cdot N(SO_3K)_2 + Me_2SO_4 \longrightarrow MeO \cdot N(SO_3K)_2 + MeHSO_4$

(iv) $MeO \cdot N(SO_3K)_2 + 2H_2O \longrightarrow MeO \cdot NH_2 + 2KHSO_4$
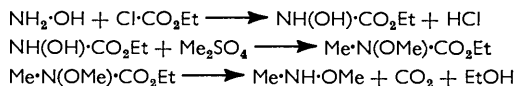
The yield of disulphonate (ii) is poor and the methylation (iii) proceeds in cold alkaline solution. The free base (iv) is liberated by potassium hydroxide and distilled in steam, being carefully trapped in ice-cold hydrochloric acid. After evaporation and recrystallization from ether–ethanol the hydrochloride melted at 148°. The latter is treated with saturated aqueous sodium hydroxide in a small well-cooled flask which is gradually heated on a water-bath. The vapour passes through a column packed with sodium hydroxide pellets at 80°; repetition of this distillation gives a liquid of b. p. 48—49° (lit.,[2] 48·1°).

*N*-Methylhydroxylamine was obtained as its hydrochloride by Beckmann's method of reduction of methyl nitrate below 15°,[17] and recrystallized from ethanol–ethyl acetate until of m. p. 87°. Beckmann's procedure for separating the free base was found to be inefficient. The *dry* methanolic solution of the base (hydrochloride + NaOMe and filter) was placed in a small Claisen flask, an ice-cooled condenser attached, and the methanol slowly distilled through at *ca.* 25 mm. to a receiver in acetone–carbon dioxide. The solid residue subsequently was distilled to a new receiver on gently raising the temperature to 60° at 15 mm. Several such distillations failed to raise the m. p. above 38° (Beckmann gives 42°) but this agreed with that given by American workers [2] (38·5°).

The product was kept in a refrigerated desiccator and handled in a dry-box. Any specimen kept at room temperatures for 24 hr. or more was redistilled before use.

*ON*-Dimethylhydroxylamine was prepared *via* hydroxyurethane [16a] which was methylated: [18]

$NH_2 \cdot OH + Cl \cdot CO_2Et \longrightarrow NH(OH) \cdot CO_2Et + HCl$

$NH(OH) \cdot CO_2Et + Me_2SO_4 \longrightarrow Me \cdot N(OMe) \cdot CO_2Et$

$Me \cdot N(OMe) \cdot CO_2Et \longrightarrow Me \cdot NH \cdot OMe + CO_2 + EtOH$

The fraction of *ON*-dimethylhydroxyurethane distilling at 150—155°/750 mm. was hydrolysed with potassium hydroxide in 50% ethanol and steam-distilled into ice-cold hydrochloric acid. Recrystallized from ethanol–ether, the hydrochloride had m. p. 115—116°. The free base (b. p. 42—43°) was obtained by the same procedure as for *O*-methylhydroxylamine but with potassium instead of sodium hydroxide.

*NN*-Dimethylhydroxylamine was prepared as its hydrochloride from ethyl nitrate: [19] m. p. after recrystallization, 103—106°. Bissot, Parry, and Campbell's prodecure using sodium-dried liquid ammonia was found the most efficient to separate the base: b. p. 100° (lit.,[2] 100·7°).

Trimethylhydroxylamine was obtained by methylation of the *ON*-dimethyl compound.[20] Phenyl isocyanate was used in separating the product, and dry hydrogen chloride was passed slowly, with cooling, into the ethereal distillate; recrystallized from ethanol–ether, the hydrochloride had m. p. 123°. This was placed on top of a few ml. of saturated aqueous potassium

[15] See Grubb-Parsons' Manual.
[16] (a) Jones, *Amer. Chem. J.*, 1898, **20**, 40; (b) Rashig, *Ber.*, 1907, **40**, 4580.
[17] Beckmann, *Annalen*, 1909, **365**, 204.
[18] Major and Fleck, *J. Amer. Chem. Soc.*, 1928, **50**, 1479.
[19] Hepworth, *J.*, 1921, **119**, 255.
[20] Jones and Major, *J. Amer. Chem. Soc.*, 1928, **50**, 2742.

hydroxide frozen by acetone–carbon dioxide in a small flask connected through an inverted U-shaped condenser-tube to a vapour trap containing anhydrous baryta. The latter was cooled to $-20°$, and the reaction flask warmed gently to about $30°$ after the system had been sealed under vacuum. After separation of the free base in this way, it was stored for 24 hr. over the drying agent and redistilled *in vacuo*: its normal b. p. was 29—30° (lit.,[2] 30°).

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