565. *Hydrogen Bonding in Gaseous Mixtures. Part V.* Infrared Spectra of Amine–Alcohol Systems*

By D. J. Millen and J. Zabicky

Gas-phase hydrogen bonded complexes formed by methanol with ammonia, methylamines, and aziridine have been detected. The O–H stretching bands in their infrared spectra are found to show a distinctive structure, qualitatively similar to that previously found for complexes formed by hydrogen halides with ethers. In general there is a strong central band with a subsidiary band on both the high and low frequency sides. An interpretation of the structure in terms of Fermi resonance is inadequate without invoking *ad hoc* features for individual complexes. On the other hand, the interpretation of the side bands as sum-and-difference bands of the O–H stretching vibration with the hydrogen bond stretching vibration offers a general interpretation. For the methanol trimethylamine complex this interpretation receives support from an independent observation by Ginn and Wood [1] of an absorption band in the far-infrared spectrum at 142·6 cm.$^{-1}$. Within experimental error, this is the frequency predicted by the sum-and-difference band assignment. It leads to a value of *ca.* 0·25 md/Å for the stretching force constant of the hydrogen bond in the trimethylamine complex.

The hydrogen bonded complexes considered in earlier Papers of this Series have involved hydrogen halides as proton donors. The work described in this Paper was begun partly with the object of testing whether or not the same general features appear in the spectra

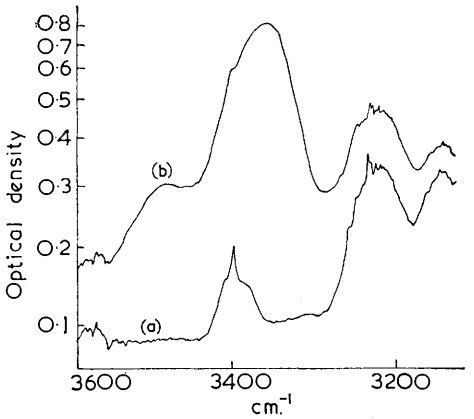

Figure 1*a*. Spectrum (*a*) is that of trimethylamine at 290 mm. pressure, and (*b*) that of a mixture of trimethylamine (290 mm.) and methanol (70 mm.). Both spectra refer to 10 cm. path length

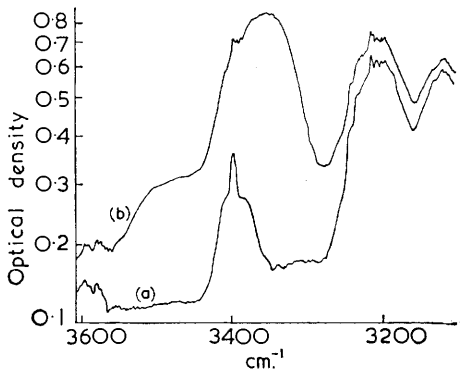

Figure 1*b*. Spectrum (*a*) is that of trimethylamine at 580 mm. pressure, and (*b*) that of a mixture of trimethylamine (580 mm.) and methanol (35 mm.). Both spectra refer to 10 cm. path length

of complexes in which the acidic part of the complex is a polyatomic molecule having several normal co-ordinates in place of a single one. The investigation of hydrogen bonding through the O–H group in the case of methanol which is described in this Paper and of nitric acid, which is reported in Part VI, indicate that the qualitative spectral features of hydrogen bonded complexes are in fact probably general, though there are some interesting quantitative differences between different complexes.

Although gaseous complexes are formed between methanol and ether,[2] it is convenient

* Part IV, J. E. Bertie and D. J. Millen, *J.*, 1965, 514.

[1] S. G. W. Ginn and J. L. Wood, *Nature*, 1963, **200**, 467.

[2] R. G. Inskeep, F. E. Dickson, and J. M. Kelliher, *J. Mol. Spectroscopy*, 1960, **4**, 477.

for these studies to use stronger bases. Comparatively strong complexes are formed with ammonia and its alkyl derivatives.[3] The complexes formed by methanol with ammonia, methylamines, and aziridine have been examined, that with trimethylamine being studied in most detail.

The Spectra.—Typical spectra of mixtures of methanol and trimethylamine are shown in Figures 1*a* and *b*. The absorption which is attributed to the hydrogen-bonded complex, shown in Figure 2, was obtained by taking the differences of optical densities. Only the optical density of the amine has been considered, since methanol has only slight absorption

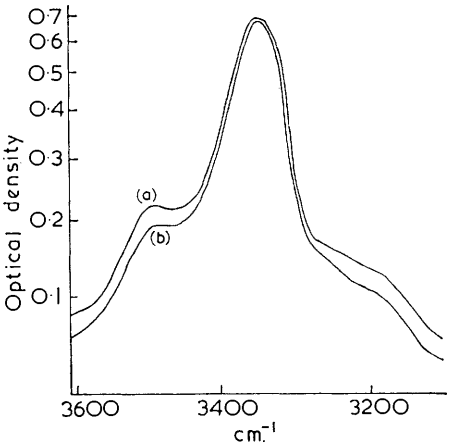

FIGURE 2. Absorption bands of the hydrogen-bonded complex. *a* and *b* refer to difference spectra obtained, as described in the text, from the spectra illustrated in Figures 1*a* and 1*b*, respectively

in the region involved. Except for the small effect due to methanol absorption, it would be correct to attribute this difference to the complex if the amine in the complex had the same absorption as the free amine. There will probably be small differences between the vibrational frequencies of the free and bound amines and some change in band envelopes, but this will not lead to serious error in any case, since, as shown below, only a relatively small proportion of the amine is present as complex. For the spectra in Figure 1, for example, it is estimated that only about 3% of the amine is present in the hydrogen bonded form (as estimated from changes in the optical density of the free O–H stretching band).

It is seen that the spectrum of the complex consists of a strong central peak, with another band on the high frequency side and a shoulder on the low frequency side. The exact shape of the absorption contour on the low frequency side is the more difficult to determine exactly, because of fairly strong C–H stretching bands in this region. The optical density measured at the maximum of the central peak was found to be proportional to the product of amine and methanol vapour pressures and may therefore be attributed to the formation of a 1 : 1 complex with an equilibrium constant K_1.

$$Me_3N + MeOH \rightleftharpoons Me_3N \cdots H{-}O{<}^{H}_{Me} \qquad K_1$$

The possibility that the side bands at 3495 and 3200 cm.$^{-1}$ might be associated with the formation of a 1 : 2 complex having two hydrogen bonds per unit was considered.

$$Me_3N + 2MeOH \rightleftharpoons Me_3N \cdots H{-}O{<}^{H\cdots O{-}Me}_{Me} \qquad K_2$$

It was not possible to explore the intensity variation over as wide a pressure range as would have been desirable because of the limitation imposed by the low volatility of methanol. Nevertheless the evidence makes it unlikely that the formation of a second complex is the correct interpretation of these bands. It was found that for various mixtures between

[3] D. J. Millen and J. Zabicky, *Nature*, 1962, **196**, 889.

the pressure ranges of 700 mm. of amine and 30 mm. of methanol to 300 mm. of amine and 70 mm. of methanol the peak intensity ratio of the bands at 3495 and 3350 cm.$^{-1}$ is approximately constant at a little over three. Figure 1 compares, for example, the spectrum of a mixture of 290 mm. of trimethylamine and 70 mm. of methanol with that of 580 mm. of amine and 35 mm. of alcohol. The spectra are seen to be qualitatively similar and Figure 2 confirms this. The absorption due to trimethylamine in each case is shown below. When allowance is also made for the weak absorption band of methanol in the

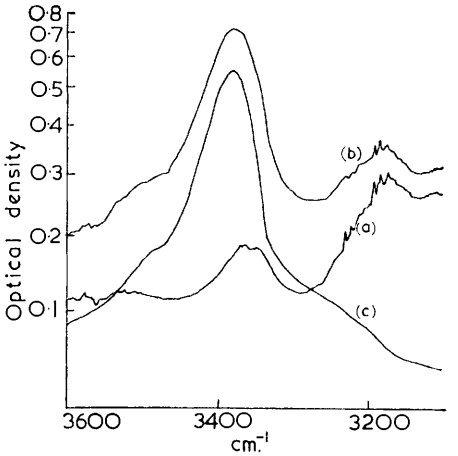

FIGURE 3. Spectra related to the dimethylamine–methanol complex: (*a*) dimethylamine (290 mm.), (*b*) mixture of dimethylamine (290 mm.) and methanol (70 mm.), (*c*) difference spectrum attributed to dimethylamine-methanol complex. All spectra refer to 10 cm. path length

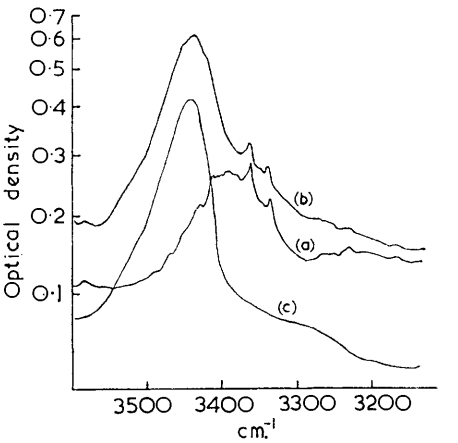

FIGURE 4. Spectra related to the methylamine–methanol complex: (*a*) methylamine (360 mm.), (*b*) mixture of methylamine (360 mm.) and methanol (90 mm.), (*c*) difference spectrum attributed to methylamine–methanol complex

region 3200—3400 cm.$^{-1}$ the difference spectra for the two mixtures are closely similar. Certainly the intensity ratio of the bands at approximately 3495 cm.$^{-1}$ for the two mixtures is not far from unity, whereas a factor of 2 might be expected in this case if the source of these bands were the 1 : 2 complex.

The spectra of mixtures of dimethylamine and methanol demonstrate the formation of a hydrogen bonded complex in much the same way as for trimethylamine. A typical example of the results obtained is shown in Figure 3, which compares the spectrum in the region 3100—3650 cm.$^{-1}$ (*a*) of dimethylamine with (*b*) that of the same sample after admitting methanol vapour into the cell. The difference spectrum (*c*) is attributed to a hydrogen-bonded complex as before. Side bands appear on both the low and high frequency sides of the main absorption peak. The high-frequency band is not as well resolved as that for the trimethylamine complex, but except for this there is qualitative similarity between the two cases. Methylamine also forms a gaseous complex with methanol as shown by Figure 4, a typical difference spectrum. A side band on the low frequency side is clearly seen; the high frequency side is more difficult to investigate because of its approach to the free methanol band. A similar band was found to occur form ethanol–ammonia mixtures having a maximum at 3510 cm.$^{-1}$. Mixtures of methanol and aziridine show a complex is formed with an absorption maximum at approximately 3460 cm.$^{-1}$. The low optical density of the band of the complex suggests that some condensation occurs on mixing.

Some further evidence comes from a comparison of the spectra of protium and deuterium bonded complexes. The absorption of the complex formed between deuteromethanol and trimethylamine was found to have its main peak at 2500 cm.$^{-1}$. A low frequency side band

is seen at very approximately 2370 cm.$^{-1}$, but absorption in this region makes it difficult to observe this band and unfortunately impossible to find whether or not there is a corresponding high-frequency side band. The remaining amines were found to undergo isotopic exchange with deuteromethanol. The gases appeared to have equilibrated by the time a spectrum could be recorded. Consequently only weak bands of deuterium bonded complexes were obtained. By using dimethyldeuteroamine, the absorption in the region 2350—2650 cm.$^{-1}$ was found to have the familiar contour (Figure 5), having a central peak at 2500 cm.$^{-1}$ and a low-frequency side band at 2370 cm.$^{-1}$. The frequencies of the O–H and O–D stretching bands of the various complexes are summarised in the Table.

Discussion.—The spectra show that there is a general qualitative similarity of the absorption band contour associated with the O–H stretching frequency of the methanol–amine complexes and those of the hydrogen stretching mode for ether–hydrogen halide complexes. There is a strong central peak with absorption bands on both the high and low frequency sides. This suggests that this type of band contour may be a fairly general feature of the spectra of hydrogen-bonded complexes in the gas phase. A general explanation of the observation can be offered in terms of sum and difference bands.

Before this interpretation is explored further it is convenient to examine briefly the

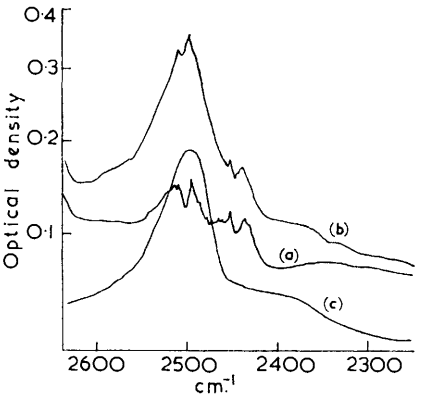

FIGURE 5. Spectra related to the deuteromethanol–dimethyldeuteroamine complex: (*a*) dimethyldeuteroamine (175 mm.), (*b*) mixture of dimethyldeuteroamine (175 mm.) and deuteromethanol (90 mm.), (*c*) difference spectrum attributed to the complex

possibility of an explanation in terms of Fermi resonance which has often been invoked for broad bands of hydrogen-bonded materials. It was shown conclusively in Part I [4] that for ether–hydrogen chloride complexes the additional bands adjacent to the main peak cannot be attributed to a Fermi resonance interaction. From the present spectra it is found that a perturbation of this kind is inadequate without special qualifying restrictions to account for the band contours observed for the various amine–methanol complexes. Thus for the trimethylamine complex there is a band of the free base at 3400 cm.$^{-1}$ which by Fermi resonance intensification and displacement by about 100 cm.$^{-1}$ might conceivably be advanced as an explanation of the high-frequency component at 3495 cm.$^{-1}$ found for the complex. The low-frequency band might be attributed to intensity enhancement of the amine band at about 3200 cm.$^{-1}$ but this time without significant displacement. On the other hand for dimethylamine, as reference to Figure 3 shows, the situation is reversed. The central peak is displaced less from the free O–H absorption band and an amine band of moderate intensity now falls on the low frequency side. The Fermi resonance interpretation would have to invoke a very considerable intensity enhancement of the very weak band on the high frequency side without displacement while on the low-frequency side this time it would require some enhancement of intensity and displacement of the frequency. Then again a further example of the difficulties of adapting a Fermi resonance interpretation is provided by the methanol–dimethyldeuteroamine complex (Figure 5) where the same spectral features are observed,

[4] J. E. Bertie and D. J. Millen, *J.*, 1965, 497.

although the levels available for Fermi resonance are quite different. We may therefore conclude that while Fermi resonance may make some contribution to the intensity of the side bands in some cases, it does not provide a general explanation for what appears to be a general phenomenon.

On the other hand the sum-and-difference-band interpretation already discussed for the ether–hydrogen halide complexes and briefly explored for methanol–amine complexes does provide a general explanation. The strong central peak found in the spectra of complexes B · · · H–OMe may be assigned to the O–H stretching frequency (ν_3) of the complex and the high and low frequency side bands may be assigned respectively as sum and difference bands of ν_3 with a low frequency vibration of the complex. The most likely low frequency vibration of the complex to be involved appears to be ν_1 the stretching vibration of the hydrogen bond. The difference band is not resolved, but from the sum band we obtain, neglecting anharmonicity, a value of 145 cm.$^{-1}$ for the low-frequency vibration of the complex.[3] The recent observation of Ginn and Wood [1] of a band at 142·6 cm.$^{-1}$ in the absorption spectrum of gaseous mixtures of trimethylamine and methanol provides strong support for the sum-and-difference band assignment. For the other amines the side bands appear only as shoulders and it is not possible to estimate their frequencies sufficiently well to determine the low frequency vibration of the complex. The difficulty of resolution may arise from a lower value for this frequency in these cases. If the displacement $\Delta\nu$ of the OH stretching frequency from the free methanol value is used as a criterion of hydrogen bond strength then, as the Table shows, increasing methylation leads to increasing bond strength. Thus it might reasonably be expected that the

Frequencies (cm.$^{-1}$) of absorption maxima of O–H stretching bands of hydrogen-bonded complexes formed by methanol with ammonia and its derivatives

	Me_3N	Me_2NH	Me_2ND	$MeNH_2$	NH_3	$[CH_2]_2NH$
(a) Complexes with methanol						
ν_3	3350	3380	—	3445	3510	3460
$\Delta\nu_3$	330	300	—	235	170	220
(b) Complexes with deuteromethanol						
ν_3	2500	2510	2500	—	—	—
$\Delta\nu_3$	220	210	220	—	—	—

highest value of ν_1 would be obtained for the complex formed by trimethylamine. By following the same procedure as in Part I [4] the stretching force constant for the hydrogen bond may be calculated. For the trimethylamine complex it is found to be about 0·25 md/Å. The value is approximate because in the absence of further information it is not possible to allow for the cross term which may well be appreciable in the potential function linking the stretching of the two bonds. The ratio of the isotopic frequencies is not very different for the complexes (trimethylamine 1·340; dimethylamine 1·347) from that for free methanol (1·354). This result lends further support to the view that the hydrogen bond is not unusually anharmonic in this sense. On the basis of the simple model of the hydrogen bond provided by the three mass system Y · · · H–X, which was discussed in Part IV,[5] this implies that the term $K_{333}Q_3^3$, and therefore probably $k_{333}r_3^3$ also, is not very different for free and hydrogen bonded groups.

An attempt was made in this connection to observe the first overtone of the O–H stretching vibration of the complex which is allowed by anharmonicity. Even in the most favourable case of trimethylamine and methanol at 660 and 80 mm., respectively, in a 10-cm. cell no band could be detected, although the overtone of free methanol was observed in the spectrum. It is concluded that either this band, unlike the fundamental, is not enhanced in intensity on complex formation or alternatively that the broadening is much greater than for the fundamental.

[5] J. E. Bertie and D. J. Millen, *J.*, 1965, 514.

Experimental

All the spectra were recorded on a Unicam S.P. 100 infrared spectrometer using a cell of 10-cm. path length. The sampling procedure was as follows. The base was introduced into the evacuated cell and its pressure recorded. The sample was condensed in a side arm and closed off from the cell by a tap, after recording its spectrum. Methanol was then admitted to the cell until the required pressure was attained, and its spectrum recorded. The contents of the side arm were then warmed to room temperature and admitted to the cell. The turbulent entry of the gases ensured good mixing. The volume of the side arm was sufficiently small that the recorded partial pressures required no significant correction. The spectra of methanol, base, and mixture were recorded successively by using this procedure.

Ammonia and methylamine were taken directly from cylinders (purity, 99% or better). Dimethylamine and trimethylamine were B.D.H. laboratory reagents supplied in sealed ampoules. Dimethyldeuteroamine was prepared by dissolving dimethylammonium chloride in deuterium oxide, followed by the liberation of the deuterated base with calcium oxide obtained by burning calcium in a current of dry oxygen. Methanol was obtained by refluxing absolute methanol twice over magnesium turnings and distilling in a water-free atmosphere. Deuteromethanol was prepared from deuterium oxide and magnesium methoxide; the deuteromethanol contained 24 mole-% of methanol but this was unimportant for the work described. Aziridine was prepared from 2-aminoethyl-sulphuric acid by following previously described procedures.[6]

We are grateful to the Friends of the Hebrew University of Jerusalem for a grant to one of us (J. Z.).

William Ramsay and Ralph Forster Laboratories,
University College, Gower St., London W.C.1.

[Present address (J. Z.): Department of Chemistry,
Instituto Venezolano de Investigacions Cientificas,
Apartado 1827, Caracas, Venezuela.] [*Received, September 10th*, 1964.]

[6] C. F. H. Allen, F. W. Spangler, and E. R. Webster, *Org. Synth.*, 1950, **30**, 38.