Hydrogen Bonding by Water in the Vapour Phase: Infrared Spectroscopic Detection of Acceptor and Donor Complexes

By M. A. HUSSEIN, D. J. MILLEN,* and G. W. MINES

(*William Ramsay and Ralph Forster Laboratories, University College, London, W.C.*1)

Summary Hydrogen bonding by water in the vapour phase as a donor to amines and as an acceptor towards 1,1,1,3,3,3-hexafluoropropan-2-ol has been detected by i.r. spectroscopy.

HYDROGEN-bonded complexes in the vapour phase have now been detected spectroscopically for proton donors ranging from strong acids to alkanols, and for proton acceptors which include amines, ethers, alcohols, and ketones. These observations suggest that the water molecule may take part in vapour-phase hydrogen bonding both as an acceptor and as a donor molecule. We now report the detection of examples of both kinds of complex.

Spectra of mixtures of water vapour and trimethylamine contain a band centred at approximately 3375 cm^{-1}, not present in either pure component. The Figure shows a typical spectrum; absorption by trimethylamine in this region is shown in spectrum (a), and that of the mixture of water vapour and trimethylamine by spectrum (b). Water vapour, as spectrum (c) shows, absorbs negligibly in this region under these conditions and the difference spectrum is given by curve (d). The band may be compared with that at 3350 cm^{-1} for vapour-phase mixtures of methanol and trimethylamine:[1] it is broad and appears to have a similar contour showing a central component with a shoulder on either side. By analogy it is assigned as an OH-stretching vibration of a hydrogen-bonded complex formed between water and trimethylamine. Mixtures of other alkyl amines and water vapour also form complexes as shown by absorption in approximately the same region, though the bands are frequently partly obscured by other absorption bands. The spectrum of 2-methylpyridine is reasonably free of absorption in this region and mixtures with water vapour show clearly an additional band centred at about 3450 cm^{-1} which is assigned as for the trimethylamine–water complex. For pyridine itself a band can be located, less accurately, at 3480 cm^{-1}. In this case comparison can be made with observations on the 1 : 1 pyridine–water complex in carbon tetrachloride solution for which a frequency of 3390 cm^{-1} has been reported.[2]

By using a balancing technique the absorption of trimethylamine in mixtures with water vapour may be compensated by trimethylamine absorption in the reference beam. The technique not only confirms the presence of the fairly broad absorption at 3375 cm^{-1} for the mixture, but also confirms a weak but sharper absorption band at approximately 3720 cm^{-1} which is also indicated in spectra observed without compensation. This band may plausibly be assigned as the remaining OH-stretching frequency of the complex, corresponding to the asymmetric stretching frequency of free water at 3756 cm^{-1}. The so-called dangling OH-vibration has been observed for 1 : 1 hydrogen-bonded complexes formed by water and a range of bases in carbon tetrachloride as solvent.[2] The frequency observed does not appear to vary much with the nature of the base. Under these conditions it is observed in the range 3685 ± 5 cm^{-1}.

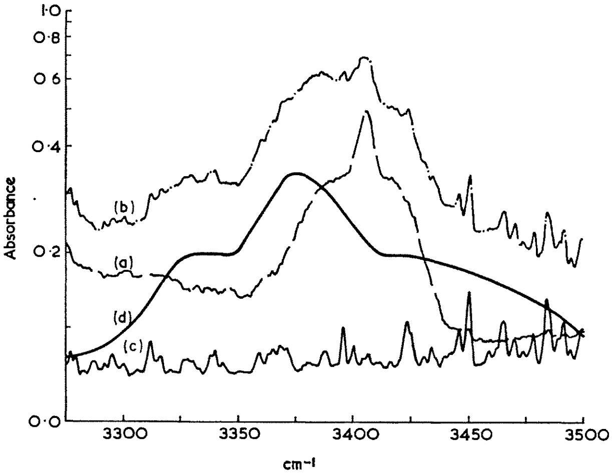

FIGURE. *Hydrogen bonding between trimethylamine and water vapour*: (a) *trimethylamine* (18 *mm*), (b) *trimethylamine* (18 *mm*) *and water vapour* (10 *mm*), (c) *water vapour* (10 *mm*), (d) *difference spectrum. Path length,* 6·25 *m.*

Mixtures of water vapour and 1,1,1,3,3,3-hexafluoropropan-2-ol [$(\text{CF}_3)_2\text{CHOH}$] show the presence of a new band which is also attributed to the formation of a hydrogen-bonded complex. In this case a very broad band is observed at about 3500 cm^{-1} being displaced towards lower frequencies, by 188 cm^{-1} from the OH-stretching band of the free alcohol. The breadth and displacement are in accord with hydrogen bonding by the alcohol to water, acting in this case as an acceptor molecule.

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