

79. *Hydrogen Bonding in Gaseous Mixtures. Part I. Infrared Spectra of Ether-Hydrogen Chloride Systems.*

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Hydrogen-bonded complexes of hydrogen chloride with various aliphatic ethers in the gas phase have been detected and investigated by means of infrared spectroscopy. The band associated with the hydrogen stretching frequency is found to be broad in each case, having a width of 400 cm^{-1} . All the bands have a similar structure, and it is shown conclusively that the structure and breadth of these bands does not arise from a Fermi-resonance interaction of the type which has often been invoked to account for the unusual breadth of the bands in the spectra of hydrogen-bonded materials. It is shown that the structure, and consequently the broadening, can be understood in terms of sum and difference bands arising from combinations of the stretching vibrations of the hydrogen-chlorine bond and the hydrogen bond. The interpretation implies a stretching force-constant of about 0.12 mdyne/\AA for the hydrogen bond in these complexes.

ALTHOUGH infrared and Raman spectra of hydrogen-bonded materials in the condensed phase have been widely studied, relatively little investigation has been made of gaseous systems. These systems provide an opportunity of obtaining a better understanding of the qualitative features of the spectra of hydrogen-bonded complexes and a possible route to the development of a quantitative understanding of certain aspects, particularly spectral intensities, molecular structure, and potential functions. Among the qualitative features, the exceptional breadth of infrared bands is probably the least well understood. Although several mechanisms have been suggested, no definite decision has been reached, from the study of condensed phases, about their relative importance or of the conditions under which each may be expected to operate.* This has been probably mainly due to complications which arise through intermolecular interaction in solid or liquid phases. The study of hydrogen bonding in the gas phase has the advantage of isolating the intramolecular contribution to the band-broadening. Infrared studies of band-broadening in gaseous systems have previously been made in only two cases, both of which suffer from special complicating features. In the first, that of carboxylic acids,³ there are two hydrogen bonds per dimer molecule in the usually accepted form, and one has also to consider the possibility of an equilibrium with the singly-hydrogen-bonded isomer.⁴ The second case of a gaseous complex is that of hydrogen fluoride; here, the spectrum of the dimer overlaps that of the monomer and is also partially obscured by bands due to tetramer and hexamer molecules.⁵

In order to examine more closely the special features of the infrared spectra of hydrogen-bonded complexes, we looked for examples of hydrogen bonding in gaseous mixtures.⁶ The present Paper is the first of a Series which reports infrared-spectral evidence of such complexes and subsequent investigations of their spectra. In this Paper, the main complexes discussed are those formed between hydrogen chloride and aliphatic ethers; complexes with deuterium chloride are discussed in Part IV of this Series.

Spectra of Mixtures of Hydrogen Chloride and Dimethyl Ether.—Spectroscopic evidence of hydrogen bonding in mixtures of hydrogen chloride and dimethyl ether is readily obtained.

* The various effects have been reviewed in refs. 1 and 2.

¹ N. Sheppard, "Hydrogen Bonding," ed. D. Hadzi, Pergamon, London, 1959, p. 85.

² G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," Freeman, San Francisco, 1960, p. 102.

³ S. Bratož, D. Hadzi, and N. Sheppard, *Spectrochim. Acta*, 1956, **8**, 249.

⁴ L. J. Bellamy, R. F. Lake, and R. J. Pace, *Spectrochim. Acta*, 1963, **19**, 443.

⁵ W. Herget, N. M. Gailar, R. J. Lovell, and A. H. Nielsen, *J. Opt. Soc. Amer.*, 1960, **50**, 1264.

⁶ J. Arnold, J. E. Bertie, and D. J. Millen, *Proc. Chem. Soc.*, 1961, 121.

In Fig. 1 the spectrum, in the region 2200—2800 cm^{-1} , of a mixture of the gases is compared with that of the unmixed gases. The third curve, C, represents the differences between the optical densities of the two spectra. Throughout the remainder of the spectrum, the procedure for taking differences led to practically complete cancellation of the ether bands. This is to be expected if either (a) the amount of ether involved in the complex were small, or (b) the intensities and envelopes of the vibration bands of the ethereal part of the complex were the same as for free ether. It is, in fact, shown in Part IV that the amount of ether present as hydrogen-bonded complex never exceeded about 10% of the total ether present. An alternative experimental procedure which led to identical band-contours for the complex was that of containing samples of the unmixed gases in a divided cell in the reference beam of the spectrometer. Using this technique, we were able to show that the band contour was insensitive to small under- or over-compensation of the ether absorption. Band contours obtained by either method may therefore confidently be regarded as those for the hydrogen-bonded complex, and to be free from significant error. It was shown from intensity measurements that the whole of

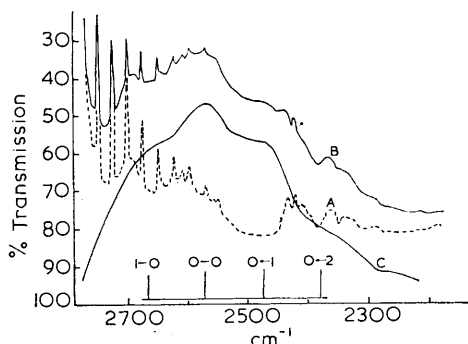


FIG. 1.

FIG. 1. Hydrogen chloride and dimethyl ether. (A) Unmixed gases. (B) Mixture: HCl, 250 mm.; ether, 125 mm.; 10-cm. path-length. (C) Subtraction spectrum.

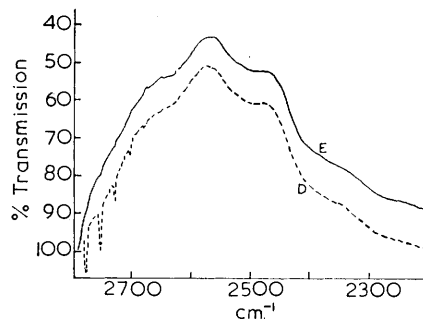


FIG. 2.

FIG. 2. Effect of changing the ratio of partial pressures. Difference spectra for two mixtures. (D) HCl, 250 mm.; ether, 125 mm. (E) HCl 125 mm., dimethyl ether, 250 mm. Path-length, 10 cm. Curve (E) has been displaced by 5% along the transmission scale. A slight unbalance, in the two beams, of the *P*-branch absorption lines of HCl is responsible for the sharp indentations on the high-frequency side.

the observed absorption bands could be attributed to a 1:1 ether-hydrogen chloride complex. In Fig. 2 a comparison is made between spectra obtained from mixtures of hydrogen chloride and dimethyl ether having partial pressures in the ratio of 1:2 and 2:1. One of the contours has been displaced by 5% along the transmission scale, in order to separate them. The two spectra are seen to be almost identical. The total intensity of the band, as will be shown in Part IV, was found to depend linearly on the product of the partial pressures of the two components. It is clear that we can exclude the possibility that part of the band contour arises from a 1:2 complex.

Comparison of the Spectra of Complexes formed by Various Ethers.—Quite similar spectra to that of the dimethyl ether complex were observed for complexes between hydrogen chloride and methyl ethyl, methyl *n*-propyl, and methyl isopropyl ethers. Fig. 3 shows the band contour for the complex formed by methyl *n*-propyl ether. For diethyl ether (Fig. 4), the peak-and-shoulders structure has virtually disappeared, but the overall width of the band is approximately the same as for the methyl ethers. The other main difference between the spectra is a slight decrease in frequency of the central peak with increasing methylation, as follows:

Ether	Me ₂ O	Me·O·Et	Me·O·Pr ⁿ	Me·O·Pr ⁱ
Frequency (cm. ⁻¹)	2570	2560	2540	2520

Some other values for central peaks are as follows:

Compound	Tetrahydrofuran	Diethyl ether	Acetone
Frequency (cm. ⁻¹)	2550	2550	2670

As Figs. 1, 2, and 3 show, the central peak is accompanied by moderately intense shoulders at *ca.* 90—100 cm.⁻¹ on each side of it. In addition there is a weaker band on the low-frequency side, in each case, at about 220 ± 20 cm.⁻¹ from the main peak. The exact shape of the band on the high-frequency side, above *ca.* 2750 cm.⁻¹, is uncertain

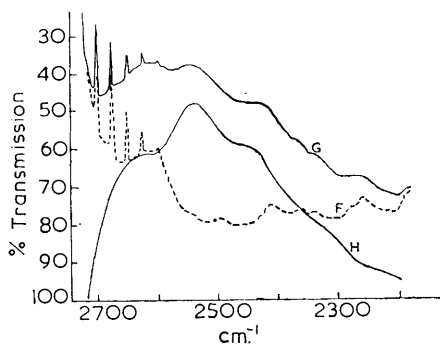


FIG. 3.

FIG. 3. Hydrogen chloride and methyl n-propyl ether. (F) Unmixed gases. (G) Mixture: HCl, 270 mm.; ether, 144 mm.; 10-cm. path-length. (H) Subtraction spectrum.

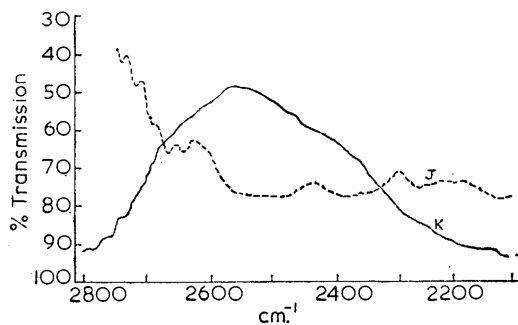
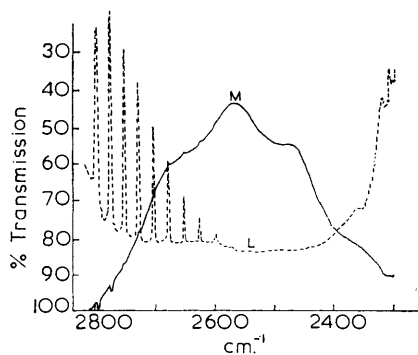


FIG. 4.

FIG. 4. Hydrogen chloride and diethyl ether. (J) Unmixed gases. (K) Difference spectrum: HCl, 242 mm.; ether, 123 mm.; 10-cm. path-length.

because of the rapidly increasing absorption in this region due to the C-H stretching vibrations. The possibility of other weak shoulders in this region cannot be excluded. For the diethyl ether complex, there is a broad featureless band having its maximum at *ca.* 2560 cm.⁻¹.

FIG. 5. Hydrogen chloride and deuterated dimethyl ether. (L) Unmixed gases. (M) Difference spectrum: HCl, 250 mm.; ether 125 mm.; 10-cm. path-length. The slight serrations on the high-frequency side arise from slight unbalance of HCl absorption in the sample and reference beams.



The spectrum, in the same range, of the complex between hydrogen chloride and deuterated dimethyl ether is shown in Fig. 5. The spectrum is seen to be very similar to that obtained for the non-deuterated compound. Again, the band contour was found to be independent of the ratio of partial pressures of the two components, confirming that the whole of the band arises from a 1 : 1 complex.

DISCUSSION

Fermi Resonance.—The most thoroughly developed theory⁷ of band-broadening for hydrogen-bonded complexes is that based on the concept of Fermi resonance. Bands arising from combination levels which happen to fall in the region of the hydrogen stretching frequency are supposed to be intensified and somewhat shifted in frequency as a result of resonance interaction. It has been suggested that potential functions for the hydrogen-bonded complexes contain unusually large anharmonic terms, and consequently there is abnormally large mixing of the vibrational states and a corresponding large Fermi-resonance enhancement of intensity. It has further been supposed that, because of this, only approximate accidental degeneracy is required, and consequently the effect may be expected to operate over a wider frequency-range than would normally be the case. Thus, for the carboxylic acids, it has been suggested that there is sufficient intensity-borrowing from the hydrogen-stretching vibration to account for the broad band at *ca.* 2500—3500 cm^{-1} . The contour of the band is attributed to the presence of several overlapping and intensified bands with sub-maxima still evident.

It seems important to consider the applicability of this theory to the present spectra. It is seen from Fig. 1 that weak bands appear in the spectrum of dimethyl ether in the neighbourhood of the hydrogen stretching frequency of the complex, and, presumably, bands of about the same frequencies are to be expected for the ether bound in the complex. In the absence of intensity-stealing, the bands for the ethereal part of the complex are expected, from their low intensities, to have negligible intensity in the observed spectrum of the complex since the proportion of ether bound in the complex is rarely more than 5% of the total ether present. The exact assignment of these combination bands is uncertain.⁸ The possibilities include binary combinations of either the symmetric C—O stretching vibration (*ca.* 930 cm^{-1}) or the asymmetric C—O stretching vibration (*ca.* 1180 cm^{-1}) with CH_3 -deformation vibrations (*ca.* 1470 cm^{-1}), leading to absorptions at *ca.* 2400 and 2650 cm^{-1} , respectively. Irrespective of whether or not this is the correct assignment, the origin of the two side-bands in the spectrum of the dimethyl ether complex, at *ca.* 2480 and 2600 cm^{-1} , might reasonably be attributed to intensification of these combinations as a result of Fermi-resonance interaction with the hydrogen-chlorine stretching frequency. However, the spectra of other complexes, taken in conjunction with those of dimethyl ether complexes, provide strong evidence against this view.

It is seen from a comparison of the spectra that, although the position of the central peak changes along the series of ethers by as much as 50 cm^{-1} , the band contour of the complex, with shoulders at about 90—100 cm^{-1} , remains qualitatively unchanged. Similarly, variations, from one ether to another, in the combination bands have no apparent effect on the spectrum of the complex. All of this evidence militates strongly against an interpretation in terms of a Fermi-resonance mechanism in the present case. Conclusive evidence is provided by the spectrum of the complex formed by deuterated dimethyl ether. The effect of deuteration is to shift the particular combination bands out of the region concerned. In fact, for the deuterated ether, the region 2450—2750 m^{-1} is happily free from absorption. Fig. 5 shows that the contour of the band of the hydrogen-bonded complex is practically the same as for the non-deuterated ether, even though the combination levels for Fermi resonance must be quite different, whether binary or ternary combinations are invoked. We may therefore conclude that the Fermi-resonance broadening mechanism does not contribute to the breadths or contour shapes of the hydrogen-stretching bands in these spectra.

Sum and Difference Bands.—The evidence shows that the band contours for the complexes formed by the series of methyl ethers are in fact comparatively insensitive to substitution within the ether molecule, including deuteration. Since the band shape is

⁷ S. Bratož and D. Hadži, *J. Chem. Phys.*, 1957, **27**, 991.

⁸ Y. Kanazawa and K. Nukda, *Bull. Chem. Soc. Japan*, 1962, **35**, 612.

independent of the vibrational frequencies of the ether, the problem is reduced to one of finding a broadening mechanism on the basis of a triatomic model $X \cdots H-Cl$. The band contour may be interpreted in terms of the two expected stretching frequencies of this model, ν_1 and ν_3 , which are essentially the stretching vibrations of the hydrogen bond and of the hydrogen-chlorine bond, respectively:



The structure of the band may be explained by means of the assignment shown in Fig. 1. The strong central peak is assigned as ν_3 , $1 \leftarrow 0$, and the approximately equi-spaced subsidiary bands are assigned as sum and difference bands of ν_1 and ν_3 . The remaining feature of the band, a weak step-out on the low-frequency side, then receives a natural interpretation as $\nu_1 - 2\nu_3$. The breadth of a band is attributed, in this interpretation, to a short progression in ν_1 accompanying the transition ν_3 , $1 \leftarrow 0$.^{7,9,10} It might be expected that the $2 \leftarrow 0$ member of the progression in ν_1 would appear in the spectrum. Experimentally, the region above 2700 cm.^{-1} is difficult to investigate, because of absorption due to both hydrogen chloride and ether, and, since reliable difference spectra could not be obtained in this region, it was not possible to ascertain whether or not there is absorption in the region where the $2 \leftarrow 0$ member would be expected. Another feature of the interpretation is that the peak intensity of the sum band is, in fact, a little less than that of the difference band. However, the ratio is determined not only by the Boltzmann factor but, among other things, by the shape of the constituent bands, which it is not possible to estimate reliably.

Although the overall width of the band, which amounts to *ca.* 400 cm.^{-1} , may be accounted for as a progression, the half-width of a constituent band of the progression, which is *ca.* 100 cm.^{-1} whatever its detailed shape, calls for further explanation. An approximate calculation of the half-width expected for the rotational envelope leads to a significantly smaller value than this. Calculations based on the assumption of a pyramidal configuration about the oxygen atom show that the complex approximates roughly to a symmetric rotor with the axis of the smallest moment in the symmetry plane. The transition concerned is expected to give rise to essentially a parallel band with a small contribution from a perpendicular component. For a parallel band the half-width has been estimated¹¹ to be *ca.* 15 cm.^{-1} , and for a perpendicular band it probably would not exceed 30 cm.^{-1} . Reasonable changes in the structure assumed for the complex, even to the extent of assuming coplanarity of the heavy atoms, will not alter these values appreciably. There must inevitably be some uncertainty in such calculations, but it seems unlikely that the half-width will exceed 30 cm.^{-1} . Part of the discrepancy between this and the observed value of *ca.* 100 cm.^{-1} must arise from the presence of hot bands. Transitions starting from levels with up to several quanta of ν_1 will contribute very significantly to the width, because of anharmonicity of the hydrogen-bond potential-function, and may, in fact, account for the whole of the width. It may be that broadening due to predissociation also contributes to the breadth, but no decision can be made from the present evidence. The observation of structure at 100-cm.^{-1} intervals allows a lower limit to be placed on the lifetime of the complex in the vibrational state with one quantum of ν_3 , *viz.*, *ca.* $3 \times 10^{-13} \text{ sec.}$ In connection with predissociation, an attempt was made to observe the overtone $2\nu_3$ of the complex, but without success. Calculations, based on intensity measurements reported in Part IV, show that, if the intensity ratio of $2\nu_3$ to ν_3 for the complex were the same as that for free hydrogen chloride,¹² namely 1 : 45, we should have easily observed the band for the complex, it having an assumed half-width

⁹ B. I. Stepanov, *Zhur. fiz. Khim.*, 1945, **19**, 507; 1946, **20**, 907; *Nature*, 1946, **157**, 808.

¹⁰ M. V. Wolkenstein, M. A. Eliashevick, and B. I. Stepanov, *Zhur. fiz. Khim.*, 1950, **29**, 1158.

¹¹ S. L. Gerhard and D. M. Dennison, *Phys. Rev.*, 1933, **43**, 197.

¹² W. S. Benedict, R. Herman, and G. E. Moore, *J. Chem. Phys.*, 1957, **26**, 1671.

as large as 400 cm.^{-1} . We conclude that either the intensity ratio for the complex is smaller than that for free hydrogen chloride or that the $2\nu_3$ band of the complex is broadened very much more than is ν_3 , perhaps by predissociation.

In the case of the diethyl ether complex, the structure of the band is much less evident than for the methyl ethers. Possibly, two or more conformations of diethyl ether are involved in bonding, and the overlapping of slightly different combination bands for the different conformers leads to a blurring of the band structure.

Force constants for the stretching of the hydrogen bonds may be evaluated if the ether molecule is regarded as a rigid body. It makes little difference whether we use a triatomic model, $\text{X-H} \cdots \text{Y}$, or a diatomic model in which only the stretching of the hydrogen bonds is considered. The value of ν_1 , estimated from the difference band, is $95 \pm 5 \text{ cm.}^{-1}$ for all the ethers employed. The changing mass of the ether molecule along the series appears to have little effect on ν_1 . On this basis, stretching force-constants for the hydrogen bonds formed by dimethyl, methyl ethyl, and methyl propyl ethers are found to be 0.11, 0.12, and 0.13 mdyne/Å, respectively. A slight increase in bond strength along the series is also indicated by the increasing displacement of ν_3 from the free hydrogen-chlorine band.

EXPERIMENTAL

Spectra.—These were recorded on a Unicam S.P. 100 grating prism instrument, using 10-cm. cells with sodium chloride windows. Spectra attributed to hydrogen-bonded complexes were obtained in two ways, and are called, for convenience, "subtraction spectra" and "difference spectra." In the former method, the spectra were obtained by filling the separate sections of a divided gas-cell with the components to be studied, recording the spectrum of the unmixed gases, and then, after mixing the gases by opening a connecting tap, recording the spectrum of the mixture superimposed on that of the unmixed gases; the subtraction spectra were obtained from the recorded optical densities. The volumes of the side-arms on the separate sections were made sufficiently similar for negligible error to be introduced on mixing the gases. Identical spectra were obtained when the ether was first confined to one section, and then expanded into the whole cell. With hydrogen chloride some difference was observed, presumably owing to pressure broadening, but because these are comparatively sharp lines, no error was introduced into the subtraction spectra. In recording difference spectra, the mixture was put into a normal 10-cm. cell and the divided cell containing the unmixed gas was inserted into the reference beam. The pressure of ether in the divided cell was initially chosen according to the relative path-length of the two cells, and finally a small adjustment was made to give cancellation on an ether band; the carbon-hydrogen stretching and methyl-group deformation bands gave identical balance-points. The balancing of hydrogen chloride was not particularly critical from this point of view.

The shapes and intensities of the bands (which show, incidentally, that the bands arise from a gaseous species and not from a condensed phase on the cell windows) were obtained, for the subtraction spectra, with a cell in which the mixture was in contact with four surfaces, while for the difference spectra there were only two surfaces. Difference spectra were recorded for several mixtures, first under conditions of deliberate over-compensation and then for conditions of under-compensation. These results showed that the difference spectra were not critically dependent on obtaining the exact compensation, and that the experimental technique gave reliable spectra for hydrogen-bonded complexes, free from significant error.

Ethers.—The non-deuterated dimethyl ether was obtained from a cylinder supplied by the Ohio Chemical Manufacturing Co. Ltd. Vapour-phase chromatography gave no indication of impurity, and the infrared spectrum agreed with that previously published.

Methyl ethyl, methyl n-propyl, and methyl isopropyl ether were prepared by Williamson's method, using a modification made by Berthoud and Brun.¹³ The purities were checked by means of gas chromatography.

Deuterated dimethyl ether was prepared as follows. Nitromethane was refluxed with a 0.02M-solution of sodium deuterioxide in 99.8% deuterium oxide for 24 hr., and the procedure repeated four times. The product was reduced by means of the method of Krause¹⁴ as

¹³ A. Berthoud and R. Brun, *J. Chim. phys.*, 1924, **21**, 144.

¹⁴ H. Krause, *Chem.-Ztg.*, 1916, **40**, 810.

modified by Noether,¹⁵ using hydrogen chloride and non-deuterated water at this stage and taking care to exclude carbon dioxide and oxygen. The [²H₃]methylamine was converted into N-[²H₃]methylbenzamide by reaction with benzoyl chloride. [²H₃]Methyl bromide was obtained from this by heating with phosphorus pentabromide in a stream of nitrogen at 160°, and [²H₃]methyl iodide was then obtained by exchange with sodium iodide in acetone. The [²H₃]methyl iodide was then converted into deuterated dimethyl ether by refluxing in acetone with silver oxide; the product had a protium content of 15%, estimated from its infrared spectrum, which was entirely satisfactory for the present requirements.

We gratefully acknowledge the award to one of us (J. E. B.) of a D.S.I.R. research studentship.

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¹⁵ H. D. Noether, *J. Chem. Phys.*, 1942, **10**, 664.
