

80. *Hydrogen Bonding in Gaseous Mixtures. Part II.*¹ *Infrared Spectra of Ether-Hydrogen Fluoride Systems.*

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Hydrogen-bonded complexes of hydrogen fluoride with aliphatic ethers in the gas phase have been detected and investigated by means of infrared spectroscopy. The main contribution to the spectrum is made by the complex R_2O, HF , although there is also evidence for $R_2O, 2HF$. The band associated with the hydrogen-fluorine stretching frequency is found to show distinct, resolvable structure. It is shown that its origin cannot be explained by means of Fermi resonance. It is suggested that the structure may be understood in terms of ν_1 and ν_3 , the stretching vibrations of the hydrogen bond and the hydrogen-fluorine bond, respectively. Bands are assigned as $\nu_3 - \nu_1$, ν_3 , and $\nu_3 + \nu_1$, and it is further suggested that the corresponding hot bands are significantly displaced because of anharmonicity. Hydrogen-bond stretching force-constants are discussed. It appears that the hydrogen bond is not unusually anharmonic so far as κ_{11} is concerned, but κ_{13} is unusually large and positive.

A preliminary study of gaseous mixtures of hydrogen fluoride with various organic substances showed the occurrence of hydrogen bonding.² Strong bands were observed for mixtures with ethers and ketones, and weaker indications of hydrogen bonding were found for mixtures with dimethyl sulphide, ethyl alcohol, and methyl fluoride, chloride, and cyanide. The spectra of mixtures of hydrogen fluoride with ethers and ketones were examined in some detail.

Spectra of Ether-Hydrogen Fluoride Complexes.—The formation of a hydrogen-bonded complex in a hydrogen fluoride-ether mixture is readily shown by the appearance of a very strong band in the hydrogen-fluorine stretching range of the spectrum. The shape of the absorption band is easily established, as there is little absorption due to the ether in this region and the main part of the absorption is well removed from the hydrogen fluoride monomer band; pressures were generally sufficiently low for absorption due to hydrogen fluoride polymers to be avoided. A typical spectrum, in the range $3100\text{--}3900\text{ cm.}^{-1}$, is shown in Fig. 1 for a dimethyl ether-hydrogen fluoride mixture. The main features are a strong band at 3470 cm.^{-1} , a band of lower intensity at 3710 cm.^{-1} , and a comparatively weak band at about 3300 cm.^{-1} . The absorption spectrum was investigated over a range

¹ Part I, preceding Paper.

² J. Arnold, J. E. Bertie, and D. J. Millen. *Proc. Chem. Soc.*, 1961, 121.

of partial pressures, in order to test whether or not the bands had a common origin. For mixtures containing an excess of dimethyl ether, the relative peak-intensities remain constant, within experimental error, over a four-fold change in the ratio of the initial partial pressure of hydrogen fluoride to that of dimethyl ether (see Table 1).

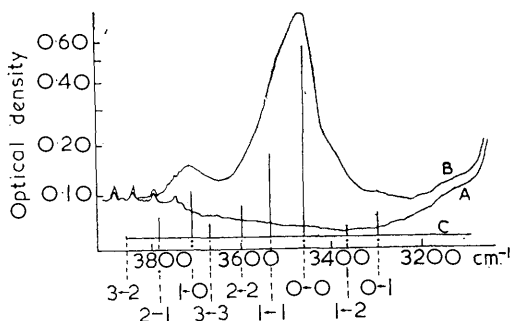


FIG. 1. Hydrogen fluoride and dimethyl ether.

- (A) Unmixed gases.
 (B) Mixture: HF, 20 mm.; ether, 80 mm.;
 10-cm. path-length.
 (C) Assignment.

The intensity ratio is further found to be essentially independent of temperature over the range 30—70°. Under these conditions, it appears that the spectrum obtained is due to a

TABLE 1.

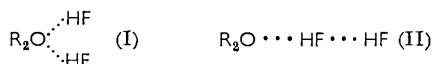
Band intensities for mixtures of dimethyl ether and hydrogen fluoride at 30°.

Initial pressure (mm.)		Optical density		O.D. (3470)
Me ₂ O	HF	3470 cm. ⁻¹	3710 cm. ⁻¹	O.D. (3710)
160	10	0.74	0.09	8.2
120	15	0.75	0.095	7.9
80	20	0.74	0.09	8.2
20	20	0.33	0.045	8.0
20	40	0.53	0.09	5.9
20	55	0.65	0.135	4.8
20	80	0.70	0.165	4.2

single hydrogen-bonded species which gives rise to all three component bands. For mixtures containing excess of hydrogen fluoride, there is some dependence of the intensity ratio on the proportions of the ether and hydrogen fluoride in the mixture (see Table 1). The intensities at 3710 and 3300 cm.⁻¹ increase relative to the main peak as the proportion of hydrogen fluoride is increased. This may be due to the increasing importance of a complex involving two hydrogen fluoride molecules:



There are two possible structures for the complex:



It is not necessary to suppose that this complex absorbs simply at 3710 and 3300 cm.⁻¹. The observations can be explained if the complex has a broad absorption band from 3100 to *ca.* 3700 cm.⁻¹. Certainly, there is an appreciably stronger low-frequency tail to the bands of mixtures which are richer in hydrogen fluoride. It seems likely that the 1 : 2 complex might well have a very broad band. For both structures (I) and (II), combination bands of two low molecular stretching frequencies with two hydrogen-fluorine stretching frequencies are possible.

The conclusion reached earlier, from the spectra of mixtures containing excess of the ether, that the 1 : 1 complex gives rise to bands at 3300, 3470, and 3710 cm.⁻¹, can be supported by semiquantitative arguments based on many observations made in the pressure

range covered by Table 1. For experimental reasons, it was not possible to determine an accurate value for the equilibrium constant, K_1 , for the complex-formation



The difficulty arises because adsorption of hydrogen fluoride on the cell walls makes measurement of the small pressures of hydrogen fluoride required here unreliable. Nevertheless, from the whole range of mixtures studied, a rough estimate of K_1 can be made, based partly on the diminution in partial pressure of hydrogen fluoride on mixing, and partly on the variation of the peak-intensity at 3400 cm.^{-1} with changing initial pressure of the components. Very approximately, we find $K_1 = 0.1\text{ (cm. Hg)}^{-1}$ and $\epsilon(3470) = 0.1\text{ cm.}^{-1}\text{ (cm. Hg)}^{-1}$. It is reasonable to assume that K_2 , for the equilibrium



is not greater than K_1 . With these equilibrium constants, it is estimated that the ratio of the amounts of 1 : 1 and 1 : 2 complex formed will vary by a factor of 20, over the pressure range covered in Table 1. The intensity ratio for the bands at 3470 and 3710 cm.^{-1}

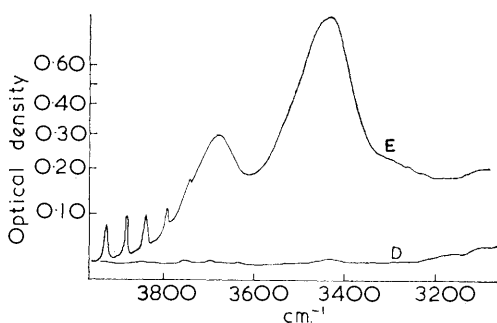


FIG. 2. Hydrogen fluoride and methyl n-propyl ether.

(D) Ether, 35 mm. (E) Mixture: HF, 35 mm.; ether, 35 mm.

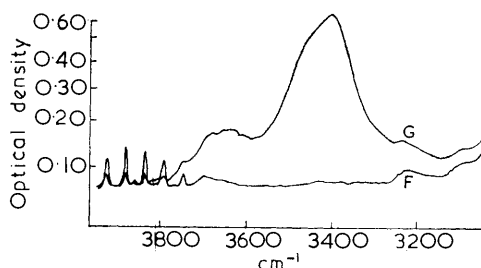


FIG. 3. Hydrogen fluoride and diethyl ether.

(F) Unmixed gases. (G) Mixture: HF, 30 mm.; ether, 50 mm.; 10-cm. path-length.

is found to change by only a factor of 2 over this range. A several-fold variation of K_2 or of K_1 in either direction does not markedly change the calculated ratio of 20. Thus, only a part of the intensity at 3710 cm.^{-1} can be attributed to a 1 : 2 complex. The spectra are largely due to a 1 : 1 complex; the spectra of mixtures containing an appreciable excess of ether are taken to provide the bands for this complex without significant distortion. The

TABLE 2.

Comparison of band-frequencies for ether-hydrogen fluoride complexes.

Complex	Frequency (cm.^{-1}) *		
	3300	3470	3710
$\text{Me}_2\text{O}, \text{HF}$	3300	3470	3710
$\text{Me}\cdot\text{O}\cdot\text{Pr}^n, \text{HF}$	3300	3435	3675
$\text{Me}\cdot\text{O}\cdot\text{Pr}^i, \text{HF}$	3250	3420	3660
$\text{Et}_2\text{O}, \text{HF}$	3225	3405	3655

* The frequencies in the first column have been estimated from a shoulder, and are approximate.

spectra of mixtures of other ethers with hydrogen fluoride are very similar to those discussed for dimethyl ether; the spectrum of a mixture with deuterated dimethyl ether is almost indistinguishable from that with the non-deuterated ether. The spectra for methyl n-propyl and methyl isopropyl ethers are very similar; the former is shown in Fig. 2. For diethyl ether (Fig. 3), the bands are somewhat broader, although the general

features are the same as for the other ethers. This observation is similar to one made for the diethyl ether-hydrogen chloride complex. The frequencies of the bands are compared in Table 2.

DISCUSSION

Qualitatively, the features of the spectra of the hydrogen fluoride complexes resemble those of the hydrogen chloride complexes, except that the side-bands, which are somewhat weaker relative to the main peak, are displaced further from it. It is shown that the Fermi-resonance interpretation of broadening is not appropriate, and that the results lend support to the sum-and-difference-band interpretation suggested for hydrogen chloride complexes in Part I.

The band associated with the hydrogen stretching vibration of the 1:1 complexes occurs in a region of the spectrum where the ethers absorb only weakly or not at all (see Figs. 1—3). The absorptions at 3710 and 3300 cm^{-1} could be attributed to Fermi resonance with combination bands of the ethereal part of the complex, only by the unlikely supposition of resonance bringing into prominence inactive or very weakly allowed

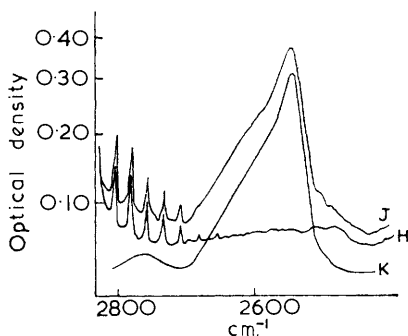


FIG. 4. Deuterium fluoride and deuterated dimethyl ether.

(H) Unmixed gases. (J) Mixture.
(K) Subtraction spectrum.

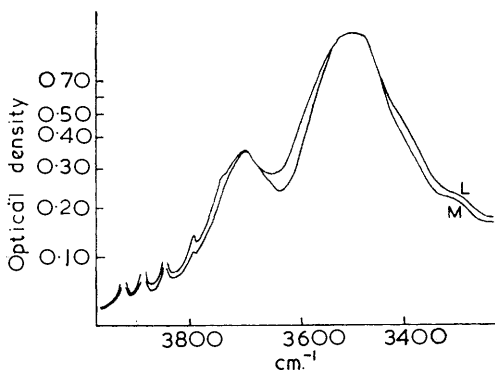


FIG. 5. The effect of temperature on the spectrum of a hydrogen fluoride-dimethyl ether mixture.

(L) 70°. (M) 30°. For conditions, see text.

transitions. That this is not the explanation is shown conclusively by the observation of identical bands for the complex formed by non-deuterated dimethyl ether and that formed by the deuterated ether, for which the combination levels available for resonance are quite different. Further evidence is provided by the spectrum of the complex of dimethyl ether with deuterium fluoride. Fig. 4 shows the spectrum of the complex of deuterium fluoride with deuterated dimethyl ether; this is more convenient, since the deuterated ether absorbs less in this region of the spectrum than does the non-deuterated ether. It is seen that the main band, at 2550 cm^{-1} , is accompanied by a weaker band on the high-frequency side, as for the hydrogen fluoride complex. This result makes it clear that the weaker high-frequency band is characteristic of the complex and is not due to an accidental resonance. The frequency-separation between the two bands for the complex with deuterium fluoride can be estimated only approximately, but is *ca.* 220 cm^{-1} for both the deuterated and non-deuterated ethers. The separation between the corresponding bands for the complex with hydrogen fluoride is *ca.* 240 cm^{-1} . The result for the complex with deuterium fluoride is of interest in another respect. If both the bands at 3710 and 3470 cm^{-1} were associated with hydrogen motion, then, on deuteration, the separation between them would

be expected to decrease by a factor of nearly $\sqrt{2}$, and this would lead to a decrease from 240 to *ca.* 170 cm^{-1} , instead of the observed separation of *ca.* 220 cm^{-1} .

Sum and Difference Bands.—The structure of the band can, in fact, be readily accounted for by combination bands quite analogous to those suggested in the interpretation for the hydrogen chloride complexes. The most intense band for the complex with dimethyl ether, at 3470 cm^{-1} , is assigned as ν_3 , essentially the hydrogen-fluorine stretching frequency of the complex



Sum and difference bands, $\nu_1 + \nu_3$ and $\nu_3 - \nu_1$, account for the next most important features, the bands at *ca.* 3710 and 3300 cm^{-1} . In the case of this complex, these ideas can be extended. The separations of the sum and difference bands from the central band are 240 and 170 cm^{-1} , respectively. The latter value is necessarily approximate, but a large anharmonicity is indicated. The most important anharmonic constant in this connection is likely to be α_{13} . If we assume that it is in fact dominant, we have $\alpha_{13} \approx 70 \text{ cm}^{-1}$. Arguments have been given which show that, for hydrogen-bonded complexes, a positive value for this anharmonic constant is probably to be expected.³ Having a value for α_{13} , we may estimate frequencies for hot bands. These are necessarily approximate, since we have neglected second-order terms in the interaction between ν_1 and ν_3 , and also contributions from α_{11} and α_{33} . Nevertheless, this assumption probably provides a rough guide to the hot bands to be expected. In Fig. 1 (A), a fairly intense spectrum of the complex, which shows its structure (B), is compared with a diagram of the hot bands to be expected in this approximation (C). The heights of the lines for the hot bands in each of the three bands have been drawn according to Boltzmann factors, but the relative heights of the three bands are arbitrarily drawn. Inclusion of the term in α_{11} would probably cause each sequence to converge to some extent. While quantitative reliance cannot be placed on the diagram, it does show that hot bands can be expected to contribute significantly to the contour of the absorption band and that the main features are in accord with the observed structure.

The effect of temperature on the spectrum is shown in Fig. 5. The upper curve is for a mixture at 70°, while the lower curve was obtained by cooling the mixture to 30° and removing sufficient of the sample to restore the peak-intensity at 3710 cm^{-1} to its original value. A relative increase in the intensity of the band at 3300 cm^{-1} is evident, in accord with its assignment as a difference band, $\nu_3 - \nu_1$. The other increases in intensity as Fig. 1(C) shows are consistent with the idea that hot bands play a significant part in determining the band shape, which shows a steep rise on the low-frequency side and a much more gradual fall-off on the high-frequency side. At the same time, the possibility cannot be excluded that part of the effect of the temperature change is to change the proportions of 1 : 1 and 1 : 2 complexes.

The hydrogen fluoride complex does not approximate quite as closely to a symmetric top as does the hydrogen chloride complex. Estimated moments of inertia are $I_a = 45.2$, $I_b = 117.7$, and $I_c = 154.7$ a.m.u. Å². Even so, the half-width of individual bands may be expected to be *ca.* 20—40 cm^{-1} . Fig. 1(C) shows that this is probably sufficient to prevent resolution of the separate combination bands, and the broadening may be explained in this way.

As in the case of the hydrogen chloride complex, we attempted to observe the first overtone of the hydrogen-fluorine stretching vibration. Even under the most favourable conditions, where the overtone of the free acid is readily observed, the overtone of the complex could not be detected. Whereas the intensity of the fundamental of the complex is several times greater than that of the free acid, the overtone of the complex is either weaker, or it may be that it is broadened even more than the fundamental, of the complex.

³ N. Sheppard, "Hydrogen Bonding," ed. D. Hadzi, Pergamon, London, 1959.

Comparison of Complexes with Various Ethers.—The interpretation of the spectra of the complexes with the other ethers is analogous to that for dimethyl ether. The calculation of the hydrogen-bond stretching force-constants cannot be made in any precise way. The difference band $\nu_3 - \nu_1$ was not resolved, and, although $\nu_3 + \nu_1$ was resolved and is known with moderate accuracy, the indications are that it is appreciably affected by anharmonicity. The following values (Table 3) have been calculated from the frequency-separation between ν_3 and the sum band. They represent effective force constants for the hydrogen-bonded complex having one quantum of hydrogen-fluorine stretching vibration.

TABLE 3.

Effective hydrogen-bond stretching force-constants (in mdynes/Å).

Dimethyl ether	0.43	Methyl n-propyl ether	0.53
Methyl isopropyl ether	0.53	Diethyl ether	0.58

The values for the ground states can be expected to be appreciably lower than these. The relative values show that the stretching force-constant of the hydrogen bond increases with increasing methylation. The displacements, $\Delta\nu$, of ν_3 from the free hydrogen-fluorine stretching frequency, also increase along the series. Both results indicate that the hydrogen-bond strength increases along the series.

The present results also allow some further comment on the potential function for the hydrogen bond. The ratio of the values of ν_3 for the hydrogen and deuterium fluoride complexes (1.36) is equal, within experimental error, to that for the free acids. The anharmonic contribution to this frequency is evidently not unusually large. On the other hand, sum and difference bands show an unusually large positive anharmonic constant, $\kappa_{13} \approx 70 \text{ cm.}^{-1}$. The effective frequency, ν_1 , increases considerably when the molecule possesses a quantum of ν_3 . This may be regarded as arising from an effective increase in hydrogen-bond strength due to the greater hydrogen stretching amplitude in this state.

The results correlate well with those for hydrogen chloride complexes. The force constants, k_1 , for the ground states are appreciably larger, as might be anticipated, hydrogen fluoride forming stronger hydrogen bonds than hydrogen chloride. The spectrum of the diethyl ether complex has broader components than have those for the other ethers. This again is quite analogous to the hydrogen chloride complex. It indicates a distinct difference between complexes of diethyl ether and those of methyl ethers. Possibly, more than one conformer of diethyl ether is involved in complex-formation, and each has slightly different combination bands.

General Conclusions.—Some implications for the interpretation of the breadths of bands observed for hydrogen-bonded materials in the liquid phase are conveniently summarised here. A number of effects have emerged which may contribute to the blurring of the banded structure, over and above any broadening mechanism specific to the liquid phase, such as that due to statistical fluctuations of environment. First, because of anharmonicity, hot bands may contribute significantly. For the hydrogen fluoride complexes, the presence of hot bands does not prevent the resolution of $\nu_1 + \nu_3$ from ν_3 , since ν_1 is large (*ca.* 200 cm.^{-1}), but for hydrogen chloride, where ν_1 is smaller (about 100 cm.^{-1}), $\nu_1 + \nu_3$ is not completely resolved. It is likely that, for the majority of hydrogen bonds, ν_1 is below 200 cm.^{-1} , and the sum and difference bands may frequently merge into the main band. Secondly, the formation of 1:2 and possibly higher complexes, each with its own sum and difference bands, is a further source of broadening through blurring of structure. In the present spectra, the 1:2 complex appears to contribute to the broadening, particularly to the low-frequency tail of the band. The origin of 1:2 or higher complexes can be considered as follows. The formation of a hydrogen bond may be expected to increase the polarity of the H-X bond, thus favouring the formation of a second hydrogen bond as in structure (II), and this will probably strengthen the first hydrogen bond by increasing the polarity still further. Thus, under certain conditions $\text{R}_2\text{O}\cdot 2\text{HF}$ with

structure (II) might be spectrally important, while the dimer $(\text{HF})_2$ might not. In general, except at high dilution or when a very poor electron-donor group X is involved, the formation of a mixture of complexes with a consequent blurring of the sum- and-difference-band structure is always a possibility. Thirdly, there is an additional blurring of structure, exemplified here by the diethyl ether complex, which may arise because of the presence of two or more conformers. Because of their low-frequency flexing vibrations, different conformers may contribute to varying extents to that normal co-ordinate which is mainly hydrogen-bond stretching, and, for this reason, the values of ν_1 may depend on the conformers, and their sum- and difference-bands will not be exactly superimposed in the spectra.

EXPERIMENTAL

Spectra.—These were recorded on a Unicam S.P. 100 grating prism instrument, using 10-cm. cells with silver chloride windows. The spectra were obtained by use of the subtraction technique described in Part I.¹ Normally, this was straightforward, since there was generally only weak absorption due to ethers in the hydrogen-fluorine stretching region. Pressure-broadening effects on the bands of the ethers were small, and no corrections were made for them. Pressures of hydrogen fluoride were normally kept below 100 mm., since, above this pressure, absorption bands due to polymers of hydrogen fluoride become important.

Chemicals were prepared and purified as described in Part I, except as described below.

Hydrogen Fluoride.—The gas was obtained directly from a cylinder obtained from Imperial Chemical Industries, Limited, and was handled in a copper and Polythene vacuum line. The maximum total impurity was stated not to exceed 1%, and no impurity band was ever observed in the infrared spectra.

Deuterium Fluoride.—This was prepared as required by exchange between hydrogen fluoride and deuterium oxide. Samples contained varying amounts of hydrogen fluoride, but this was unimportant for the present work.

Deuterated Dimethyl Ether.—Trimethyloxosulphonium iodide was prepared from methyl iodide and dimethyl sulphoxide following the procedure of Kuhn and Trischman.⁴ Following the method of Cotton *et al.*,⁵ the recrystallised product was treated with a dilute solution of potassium carbonate in 99.8% deuterium oxide at *ca.* 90° for 1 hr. After cooling the solution in ice, the crystalline product was filtered off and the procedure repeated three times. The $[\text{}^2\text{H}_3]$ trimethyloxosulphonium iodide was decomposed by heating it to 200°, and the $[\text{}^2\text{H}_3]$ -methyl iodide was collected and separated from the sulphoxide, as described by Cotton *et al.*⁵ The $[\text{}^2\text{H}_3]$ methyl iodide was converted into the deuterated ether by refluxing with a suspension of silver oxide in acetone. From the infrared spectrum, it was estimated that the product contained about 10% of protium, which was entirely satisfactory for the present purposes.

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⁴ R. Kuhn and H. Trischman, *Annalen*, 1958, **611**, 117.

⁵ F. A. Cotton, J. H. Fassnacht, W. D. Horrocks, and N. A. Nelson, *J.*, 1959, 4138.