# 81. *Hydrogen Bonding in Gaseous Mixtures. Part III.*[1] *Infrared Spectra of Complexes formed by Hydrogen Fluroide with Carbonyl and Other Compounds.*

By J. ARNOLD and D. J. MILLEN.

Hydrogen-bonded complexes have been detected in gas-phase mixtures of hydrogen fluoride with acetone, methyl ethyl ketone, and acetaldehyde by means of the strong bands which appear in the infrared spectra of these mixtures. Complexes are also reported for hydrogen fluoride with formaldehyde, methanol, methyl fluoride and chloride, methyl sulphide, and methyl cyanide. The bands for the complexes formed from carbonyl compounds have been investigated in most detail, being broad and showing structure consisting of approximately equi-spaced components. It is shown that the band structure does not arise from a Fermi-resonance interaction. As in the case of the ether complexes, the band structure can be explained as the hydrogen–fluorine stretching frequency accompanied by sum and difference bands with a low vibrational frequency of the complex. Most probably, the mode involved in this vibration is the stretching of the hydrogen bond. On this basis, the stretching force-constant of the hydrogen bond is 0·09 mdyne/Å for the complex formed from acetone.

SPECTRA of mixtures of hydrogen fluoride with a series of volatile organic compounds have been investigated, in order to extend the observations made with ethers. Of the various mixtures considered, those containing carbonyl compounds have been investigated in most detail. The spectra are in general strong, and gaseous mixtures are readily investigated, since, unlike those of hydrogen chloride and acetone, they are chemically stable.

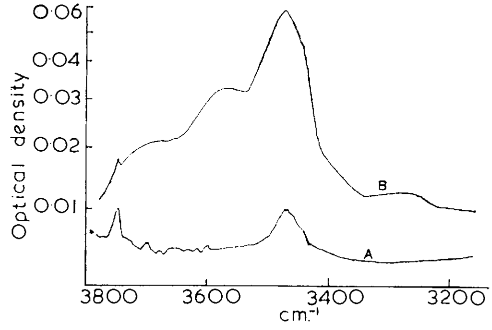

FIG. 1. Hydrogen fluoride and acetone.
(A) Unmixed gases.
(B) Mixture: HF 40 mm.; acetone, 50 mm.; 10-cm. path-length.

*Spectrum of the Hydrogen Fluoride–Acetone Complex.*—In Fig. 1, the spectrum in the region 3200—3900 cm.$^{-1}$, of a mixture of hydrogen fluoride and acetone is compared with that of the unmixed gases. The spectrum is typical of those obtained for mixtures at various partial pressures. Component bonds at *ca.* 3470, 3580, and 3700 cm.$^{-1}$ are clearly evident, and weak bands are apparent at frequencies which can be estimated only approximately as 3280 and 3380 cm.$^{-1}$. The bands, in fact, form an approximately equi-spaced series with an interval of about 100 cm.$^{-1}$. The dependence of the relative intensities of the component bands on the partial pressures of hydrogen fluoride and acetone and on the temperature was studied, in order to test whether a 1 : 2 complex, as well as a 1 : 1 complex, was responsible for part of the spectrum. The results are summarised in the Table.

As in the case of ethers with hydrogen fluoride, the partial pressures of hydrogen fluoride can be regarded only as approximate estimates, owing to adsorption. Even so, it is possible to examine the temperature- and pressure-dependence of the ratio of optical densities of two bands. The pressure range that can be studied is limited by the onset of condensation;

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[1] Part II, preceding Paper.

Temperature- and pressure-dependence of peak-intensities of component bands.

| Temper-ature | Pressure (mm.) | | Optical density | | | O.D. (3470) / O.D. (3700) | O.D. (3470) / O.D. (3580) |
|---|---|---|---|---|---|---|---|
| | $Me_2CO$ | HF | 3470 cm.$^{-1}$ | 3580 cm.$^{-1}$ | 3700 cm.$^{-1}$ | | |
| 30° | 80 | 40 | 0·47 | 0·25 | 0·16 | 3·0 | 1·9 |
| ,, | 65 | 40 | 0·46 | 0·25 | 0·15 | 3·0 | 1·8 |
| ,, | 50 | 40 | 0·49 | 0·28 | 0·16 | 3·0 | 1·7 |
| ,, | 40 | 40 | 0·46 | 0·27 | 0·17 | 2·6 | 1·6 |
| ,, | 40 | 80 | 0·39 | 0·23 | 0·16 | 2·5 | 1·7 |
| 50° | 80 | 40 | 0·55 | 0·30 | 0·21 | 2·6 | 1·8 |
| ,, | 65 | 40 | 0·42 | 0·24 | 0·15 | 2·8 | 1·8 |
| ,, | 50 | 40 | 0·37 | 0·22 | 0·15 | 2·5 | 1·7 |
| ,, | 40 | 40 | 0·34 | 0·22 | 0·15 | 2·2 | 1·6 |
| ,, | 40 | 80 | 0·37 | 0·22 | 0·15 | 2·5 | 1·7 |
| 70° | 80 | 40 | 0·39 | 0·22 | 0·15 | 2·6 | 1·8 |
| ,, | 65 | 40 | 0·28 | 0·17 | 0·11 | 2·6 | 1·7 |
| ,, | 50 | 40 | 0·23 | 0·15 | 0·10 | 2·4 | 1·5 |
| ,, | 40 | 40 | 0·20 | 0·13 | 0·10 | 2·1 | 1·5 |
| ,, | 40 | 80 | 0·26 | 0·17 | 0·12 | 2·1 | 1·6 |

presumably the complex is less volatile than either of the components. The effect is noticeable for the first entry in the Table. The intensities for this mixture are an exception, in that they are lower than those at 50°, because part of the sample condensed at the lower temperature. The results in the Table show that there is a small variation in intensity of the bands at 3580 and 3700 cm.$^{-1}$ relative to the most intense band at 3470 cm.$^{-1}$. The variation is too small to allow the high-frequency bands to be attributed to a complex, $Me_2CO,2HF$. However, the small increase in relative intensity of these bands as the proportion of hydrogen fluoride in the mixture is increased is possibly an indication that some absorption in this region is due to the 1 : 2 complex. That it is not the main cause, is confirmed by the observation that, in a mixture containing an appreciable excess of acetone (160 mm. of acetone and 20 mm. of hydrogen fluoride) the bands at both 3580 and 3700 cm.$^{-1}$ appear quite strongly and in their usual peak-intensity ratio of *ca.* 1·5. The intensity of the band at 3470 cm.$^{-1}$ cannot be estimated accurately for this mixture, because, at this pressure, a fairly strong absorption due to acetone appears at the same frequency. Change of temperature has no marked influence on relative intensities, only small changes in the bands being detected.

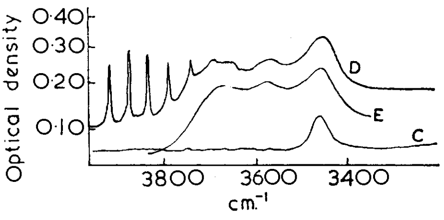


FIG. 2. Hydrogen fluoride and methyl ethyl ketone.

(C) Ketone, 50 mm.
(D) Mixture: HF, 50 mm., ketone, 50 mm.
(E) Subtraction spectrum.

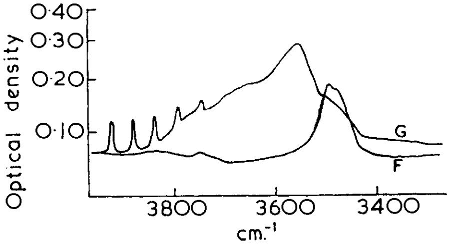


FIG. 3. Hydrogen fluoride and acetaldehyde.

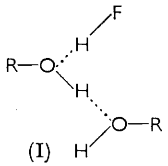
(F) Acetaldehyde, 100 mm.
(G) Mixture: HF, 40 mm.; aldehyde, 40 mm.

*Hydrogen Bonding to Other Carbonyl Groups.*—The band structure which was found in the hydrogen–fluorine stretching region for a mixture of methyl ethyl ketone and hydrogen fluoride (Fig. 2) closely resembles that for the acetone complex. There are very similar component bands at *ca.* 3465, 3580, and 3680 cm.$^{-1}$. Again, the first overtone of the carbonyl stretching frequency occurs at about the same frequency as does the strongest peak in the spectrum of the complex.

The spectra of mixtures of hydrogen fluoride with acetaldehyde (see Fig. 3) are particularly important, because here the coincidence with the carbonyl overtone is avoided;

the overtone occurs at *ca.* 3485 cm.$^{-1}$, which is *ca.* 70 cm.$^{-1}$ below the most intense band in the spectrum of the complex. However, as for other carbonyl compounds, three bands can be discerned. Their frequencies in this case are *ca.* 3555, 3655, and 3760 cm.$^{-1}$. On adding hydrogen fluoride to formaldehyde, the spectrum of the aldehyde became much weaker. Possibly, the hydrogen fluoride catalyses the polymerisation of formaldehyde, which leads to condensation. Nevertheless, a weak peak at 3560 cm.$^{-1}$, presumably due to hydrogen bonding, was observed, even at the small residual pressure of formaldehyde, but it was not possible to decide whether or not the band structure was similar to that for complexes formed by other carbonyl compounds.

*Hydrogen Bonding of Hydrogen Fluoride to Methyl Halides, Methyl Cyanide, and Methanol.*—Problems due to the appearance of a hydrogen-bonded condensed state, which were negligible for ethers and restrictive for ketones, seriously limited the study with methanol. It was found that completely gaseous equimolar systems could not be obtained at 30° when the partial pressure of each component was above *ca.* 30 mm. The liquid phase showed a very broad band extending over several hundred cm.$^{-1}$. It seems likely that both the decreased volatility and the very broad bands are due to the formation of complexes of increased size. Complexes of the type $R_2O \cdots HF \cdots HF$, in which a second hydrogen fluoride molecule is bonded to a fluorine atom which has become more electronegative as a result of hydrogen bonding, have already been discussed.[1] For alcohols, in addition to complexes of this type, structure (I) has to be considered. The formation of the methanol dimer, which is known to occur in free methanol vapour,[2] will be favoured by the increased polarity of the O–H bond, resulting from the formation of the hydrogen bond with hydrogen fluoride. So far as the gas-phase absorption is concerned, there is a peak at 3540 cm.$^{-1}$. This is a significantly smaller displacement ($\Delta\nu =$ 420 cm.$^{-1}$) from the free hydrogen fluoride frequency than was found for dimethyl ether ($\Delta\nu = 490$ cm.$^{-1}$). The low vapour pressure prevented any search for structure in the band. The study of water–hydrogen fluoride mixtures is restricted even more by low volatility. No indication of a gas-phase complex could be observed under our experimental conditions, even when the temperature was raised to 50°.



(I)

The formation of a weak complex between hydrogen fluoride and methyl fluoride is indicated by the appearance of a weak band close to the $P(3)$ line of the hydrogen fluoride monomer band. The frequency is close to that which has been assigned to the hydrogen fluoride dimer,[3] and, as in that case, because of its low intensity and obscuration by the monomer lines, the band was not easily investigated. A similar weak band, between $P(3)$ and $P(4)$, for mixtures of methyl chloride and hydrogen fluoride shows that a complex is formed in this case. Under the same conditions, no new bands were observed for mixtures with either methyl bromide or iodide. Similar weak bands have previously been reported [4] for complexes with carbon dioxide, sulphur dioxide, and carbonyl sulphide.

Mixtures of hydrogen fluoride and methyl cyanide show a band which is intermediate in intensity between that for mixtures of hydrogen fluoride with methyl fluoride and with dimethyl ether. The band, at 3660 cm.$^{-1}$, is asymmetric in the usual way, rising comparatively sharply on the low-frequency side and falling away more gradually on the high-frequency side. Again, the low volatility did not allow an examination for the presence of weaker side-bands.

The formation of a complex between dimethyl sulphide and hydrogen fluoride is indicated by the appearance of a band at *ca.* 3530 cm.$^{-1}$. Again, it was too weak for any structure to be observed. No such band was observed under the same conditions for mixtures with hydrogen sulphide.

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[2] R. G. Inskeep, J. M. Kelliher, P. E. McMahon, and B. G. Somers, *J. Chem. Phys.*, 1958, **28**, 1033.
[3] W. F. Herget, N. M. Gailar, R. J. Lovell, and A. H. Nielsen, *J. Opt. Soc. Amer.*, 1960, **50**, 1264.
[4] T. G. Burke and D. F. Smith, *J. Mol. Spectroscopy*, 1959, **3**, 381.

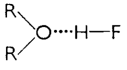
## DISCUSSION

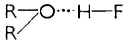
The spectra of hydrogen fluoride complexes with carbonyl compounds are characterised by three main peaks in the hydrogen–fluorine stretching region. For the acetone complex (Fig. 1) the bands occur at 3470, 3580, and 3700 cm.$^{-1}$. The strongest of those is almost coincident with the first overtone of the carbonyl stretching vibration. There is evidence from two sources that the band at 3470 cm.$^{-1}$ does not, however, arise from Fermi-resonance intensity-enhancement of the overtone band. First, the same general band-shape shown by both the acetone and methyl ethyl ketone complexes is found for that of acetaldehyde (Fig. 3), where the coincidence with the carbonyl overtone does not occur. The conditions for Fermi resonance in the two cases are quite different, but there is no change in the general appearance of the band except for the different position of the carbonyl overtone. Secondly, the spectrum of the complex formed by deuterium fluoride with acetone has its main peak at 2560 cm.$^{-1}$. If the band at 3470 cm.$^{-1}$ is taken to be the counterpart of this in the hydrogen fluoride complex, then the isotopic frequency-ratio is 1·36, identical with that for the ether complexes. On the other hand, if the band at 3470 cm.$^{-1}$ is attributed to Fermi-resonance enhancement of the carbonyl overtone, leaving that at 3580 cm.$^{-1}$ to be assigned to the hydrogen stretching frequency of the complex, the unlikely isotopic frequency-ratio of 1·40 is obtained. These two pieces of evidence do not, of course, preclude the possibility that there may be some intensity-enhancement of the carbonyl overtone; however, this cannot be the main source of the band at 3470 cm.$^{-1}$.

An isotopic frequency-ratio of 1·36 in fact strengthens the suggestion, by comparison with the ether complexes, that 3470 cm.$^{-1}$ is to be assigned to the hydrogen stretching frequency of the complex. The remainder of the spectrum of the acetone complex may then be assigned as two moderately intense sum bands, $\nu_3 + \nu_1$ and $\nu_3 + 2\nu_1$, and two comparatively weak difference bands, $\nu_3 - \nu_1$ and $\nu_3 - 2\nu_1$, where $\nu_1$ is very approximately 100 cm.$^{-1}$. The most likely explanation is that $\nu_1$ is the stretching frequency of the hydrogen bond. If this is correct, we can make an interesting comparison with the spectra of the ether complexes. The displacement of the hydrogen-stretching frequency from that of free hydrogen fluoride is almost the same for both the ether and ketone complexes, *viz.*, $\Delta\nu \sim 490$ cm.$^{-1}$. On the other hand, the hydrogen-bond stretching frequencies differ considerably, being *ca.* 200 and 100 cm.$^{-1}$ for the ether and ketone complexes, respectively. This would imply that, while $\Delta\nu$ may be a useful measure of relative hydrogen-bond strengths along a series of closely related compounds, *e.g.*, ethers, it does not provide a means of comparing the strengths of hydrogen bonds formed by a given proton donor with two quite different electron donors.

An alternative assignment of the components in the spectrum of the acetone complex is that the first sum and difference bands involve a low-frequency wagging vibration associated with the hydrogen bond and the second sum and difference bands involve one quantum of the hydrogen-bond stretching vibration which, on this assignment, would be *ca.* 200 cm.$^{-1}$. Intensity considerations make this assignment seem unlikely.

It is shown in Part IV that the sum and difference bands probably derive their intensity from the anharmonic term in the potential function $k_{133}\,Q_1Q_3^2$, where $Q_1$ is the normal co-ordinate which involves mainly change in hydrogen-bond length and $Q_3$ refers to change which is confined mainly to the hydrogen–fluorine bond length. The analogous term which is expected to contribute to sum and difference bands with the wagging vibrations is $k_{233}\,Q_2Q_3^2$, where $Q_2$ is the wagging co-ordinate. For an assumed planar complex for ethers (II), this term vanishes both for the in-plane and out-of-plane vibrations, since, by symmetry, only even terms of $Q_2$ are allowed in the potential function. On general chemical grounds, the ether complex is likely to have a pyramidal structure (III), in which case this exclusion holds rigorously only for the out-of-symmetry-plane wagging co-ordinate. At the same time, it is likely that $k_{233}\,Q_2Q_3^2$ is determined largely by the local symmetry of the group O · · · H–F, and is thus, in any case, likely to be small. Therefore, even if the acetone complex should have no symmetry plane, as in structure (IV), it seems unlikely that there would be sufficiently large anharmonic terms to provide unusually high intensity for sum and difference bands involving wagging vibrations, as compared with ether complexes. However, the possibility of its importance cannot be excluded with complete certainty, since it may be [5] that, because of the form of the normal vibrations, other anharmonic terms in the potential function, besides those dependent on $r_1r_3^2$, may contribute to $k_{233}\,Q_2Q_3^2$.


(II)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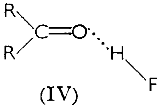
(IV)

On the basis that the stretching vibration of the hydrogen bond has a frequency of 100 cm.$^{-1}$, the stretching force-constant is 0·088 mdyne/Å.

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[5] F. R. Burden and D. J. Millen, unpublished calculations.