

**566.** *Hydrogen Bonding in Gaseous Mixtures. Part VI.<sup>1</sup>  
Infrared Spectra of Ether–Nitric Acid Systems*

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The infrared spectra of nitric acid–ether systems demonstrate the formation of hydrogen-bonded complexes. An estimate of the formation equilibrium constant has been made and the structure of the O–H stretching band examined. The complexes provide further examples of the class in which the proton donor is a polyatomic molecule having several normal co-ordinates. There is consequently an opportunity to test whether there are important contributions to the infrared band structure from Fermi resonance intensification of combination bands arising from the proton donor part of the complex, as distinct from those of the acceptor molecule which were the only ones available in the complexes formed by the hydrogen halides. It is found that, even with this additional possibility, Fermi resonance is inadequate to account for the structure of the O–H stretching band of the nitric acid ether complexes. The structure is in fact qualitatively similar to that found for other gaseous hydrogen bonded complexes. It consists of a strong central band with two less intense, approximately equi-spaced bands; one is at a lower frequency and the other at a higher frequency than the most intense band. The three bands, which occur at 2765, 3130, and 3470  $\text{cm}^{-1}$  in the case of the dimethyl ether complex, are discussed in terms of sum- and-difference bands accompanying the O–H stretching band of the complex. The bands of the complex formed by deuteronic acid with dimethyl ether are also discussed in this connection.

THE study of gas-phase hydrogen bonding between amines and alcohols, as reported in Part V,<sup>1</sup> was undertaken partly in order to examine a case where the hydrogen donor is a

<sup>1</sup> Part V, D. J. Millen and J. Zabicky, preceding Paper.

polyatomic molecule rather than a simple diatomic, as used in systems reported in earlier Parts of this Series. Nitric acid-ether systems provide another example in which the hydrogen donor is a polyatomic molecule with several normal co-ordinates. It thus offers an opportunity to test if Fermi resonance intensification of combination bands arising from the proton donor part of the complex, as distinct from the acceptor molecule, is important in contributing to the breadth of infrared bands of hydrogen-bonded complexes. It has previously been pointed out<sup>2</sup> that Fermi resonance with combination levels of the proton donor part of the complex may be more important than such resonance involving vibrational modes of the acceptor in the complex, since the former case does not require anharmonic coupling across the weak hydrogen bond.

*The Spectra.*—It has previously been briefly reported<sup>3</sup> that spectra of mixtures of nitric acid and dimethyl ether show that a hydrogen-bonded complex is formed. Some typical spectra of gaseous mixtures are shown in Figures 1 and 2. In each case spectrum (a) is that of free nitric acid, in which the most important feature for the present purpose is the strong O-H stretching band at 3560  $\text{cm}^{-1}$ ; spectrum (b) is that of free ether, and spectrum (c) is that of the mixture. Difference spectra have not been drawn because in the region around 2700  $\text{cm}^{-1}$  the strong C-H absorption band makes such spectra unreliable and in the range 3100—3600  $\text{cm}^{-1}$  the background absorption is negligible. The absorption due to the complex in this region is obvious on inspection. It is immediately evident that, as for other gaseous hydrogen bonded complexes, previously discussed, there are three absorption bands. The two higher frequency ones are clearly resolved in Figures 1 and 2 as separate peaks at 3130 and 3470  $\text{cm}^{-1}$ , while the third appears in these spectra as an incompletely resolved shoulder, at a little below 2800  $\text{cm}^{-1}$ , on the strong C-H absorption band. By taking spectra of mixtures in which the pressure of ether is continuously reduced it was found possible to resolve the low-frequency side band before the spectrum became too weak to record. From an optimum mixture of about 10 mm. of dimethyl ether and 45 mm. of nitric acid the peak was measured as 2765  $\text{cm}^{-1}$ .

*Dependence of Intensities of Partial Pressures.*—In order to test whether the three bands have the same molecular origin, the partial pressures of ether and nitric acid were varied

TABLE I  
Peak optical densities of bands at 3130 and 3470  $\text{cm}^{-1}$  in mixtures of nitric acid and dimethyl ether

Mixture	Initial partial pressure (mm.)		Optical density		
	Me <sub>2</sub> O	HNO <sub>3</sub>	3130 $\text{cm}^{-1}$	3470 $\text{cm}^{-1}$	Ratio
1	25	45	0.21	0.04	5.3
2	50	45	0.30	0.05	6.0
3	100	45	0.51	0.09	5.5
4	150	45	0.50	0.08	6.2
5	400	45	0.92	0.19	4.7
6	600	45	0.95	0.20	4.7
7	200	30	0.65	0.11	5.9
8	400	30	0.80	0.16	5.0

over as wide a range as volatility allowed. In Table I the peak optical densities of the two clearly resolved bands, 3130 and 3470  $\text{cm}^{-1}$  are listed for various initial pressures of the two gases. The last column records the ratio of the optical densities of the two bands.

For various experimental reasons the accuracy of the measurements is not high. Successive attempts for several mixtures indicate that experimental error is such that the ratio of the optical densities is probably reliable to within about 10% of its value. Within this approximation the ratio is approximately the same for all mixtures examined, having a value of about 5.5 over a twenty-five fold range of partial pressure ratio. The position is illustrated in Figures 1 and 2 which show that the spectrum obtained from a mixture of

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

<sup>3</sup> D. J. Millen and O. A. Samsonov, *Chem. and Ind.*, 1963, 1694.

200 mm. of ether and 30 mm. of nitric acid closely resembles that for a mixture of 100 mm. of ether and 45 mm. of nitric acid. These indications that the bands have the same origin can be extended to obtain semi-quantitative support for this view. It is seen from Table 1 that increasing the partial pressure of ether from 400 to 600 mm. has only a small effect on the intensities. The reason for this is that almost the whole of the nitric acid in these mixtures is present as complex. No separate O-H stretching band at  $3560\text{ cm}^{-1}$  for free nitric acid is observed for these two mixtures; the tail of the band due to the complex at  $3470\text{ cm}^{-1}$  overlaps this region and so it cannot be established that the absorption due to free OH is below the level of detection, but it is certainly quite small. We may therefore obtain, to a good approximation, the peak extinction coefficient of the band at  $3130\text{ cm}^{-1}$

FIGURE 1. Spectra related to the dimethyl ether-nitric acid complex: (a) dimethyl ether (200 mm.), (b) nitric acid (30 mm.), (c) mixture of dimethyl ether (200 mm.) and nitric acid (30 mm.) 10 cm. path length

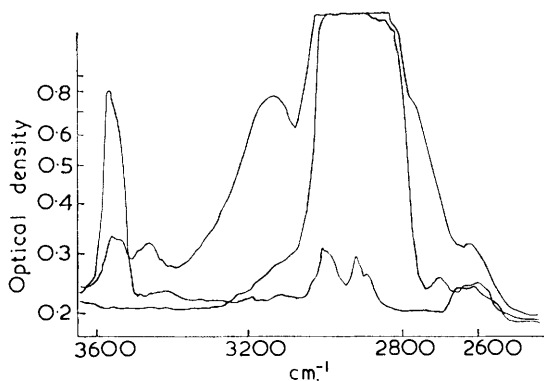
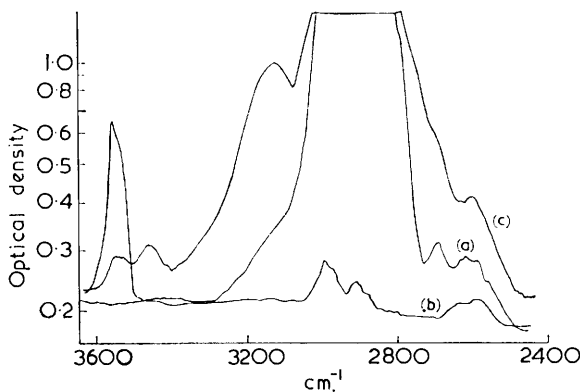
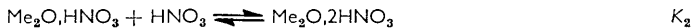


FIGURE 2. Spectra related to the dimethyl ether-nitric acid complex: (a) dimethyl ether (100 mm.), (b) nitric acid (45 mm.), (c) mixture of dimethyl ether (100 mm.) and nitric acid (45 mm.). 10 cm. path length

$\text{cm}^{-1}$  by assuming that under these conditions the whole of the nitric acid is involved in complex formation. From the extinction coefficient, the intensities of the band in the spectra of mixtures for which complex formation is less complete can be used to obtain the equilibrium constant  $K_1$ , for complex formation.



The value obtained,  $K_1 = 2 \times 10\text{ mm}^{-1}$ , is approximate but entirely satisfactory for the present discussion. It allows us to consider whether the 1 : 2 complex



with a formation constant of  $K_2$ , can be accommodated by the intensities of the bands in Table 1. If we suppose  $K_2 = K_1$  then a sixfold variation in the ratio of the partial pressures of the 1 : 1 and 1 : 2 complexes is to be expected over the range of partial pressures covered in Table 1, whereas no significant variation in the intensity ratio of the two bands is observed. Furthermore in passing from one mixture to another, the changes in some cases

are in the opposite direction to expectation on the assignment of the band at  $3130\text{ cm.}^{-1}$  to the 1 : 1 complex and  $3470\text{ cm.}^{-1}$  to the 1 : 2 complex. For instance it would be expected on this basis that in passing from mixture 2 to mixture 8 the band at  $3470\text{ cm.}^{-1}$  would decrease in intensity by a factor of about four, whereas a threefold increase is observed. Putting  $K_2 = 10K_1$  leaves both of these points qualitatively unchanged and so does putting  $K_2 = 0.1K_1$ . The intensities thus provide good evidence that the band at  $3470\text{ cm.}^{-1}$  is not to be attributed to a 1 : 2 complex. The pressure dependence of the intensity of the band at  $2765\text{ cm.}^{-1}$  cannot be investigated in the same detail because of the serious overlapping with the strong C-H stretching bond. However, like the band at  $3470\text{ cm.}^{-1}$  it appears strongly for mixtures containing a large excess of ether and so it is unlikely that it arises from a 1 : 2 complex.

TABLE 2

Frequencies of ether-nitric acid complexes ( $\text{cm.}^{-1}$ )				
Ether	(1)	(2)	(3)	$\Delta\nu$
$\text{Me}_2\text{O}$ .....	2765	3130	3470	430
$\text{MePr}^n\text{O}$ .....	shoulder *	3100	3430	460
$\text{Et}_2\text{O}$ .....	2730	3080	3420	480

\* Frequency not obtainable because of overlapping with ether absorption band.

*Summary of Frequencies of Complexes.*—The spectra of complexes formed by nitric acid with diethyl ether and methyl propyl ether were qualitatively similar as shown by the frequencies of the bands summarised in Table 2. The results show that, as for other hydrogen-bonded gaseous complexes, there is a general pattern of a strong central band with a less intense band on either side displaced by about the same frequency interval.

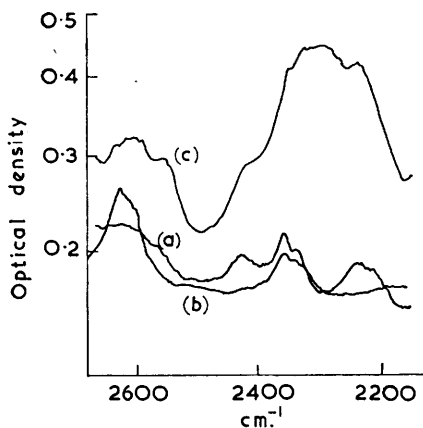


FIGURE 3. Spectra related to the dimethyl ether-deuteriogenic acid complex: (a) dimethyl ether (200 mm.), (b) deuteriogenic acid (ca. 40 mm.), (c) mixture of dimethyl ether (200 mm.) and deuteriogenic acid (ca. 40 mm.).

*Mixtures of Deuteriogenic Acid and Dimethyl Ether.*—A typical spectrum of a mixture of deuteriogenic acid and dimethyl ether is shown in Figure 3. The formation of a complex is shown by the diminution of the intensity of the O-D stretching band of the free acid and the appearance of new bands at  $2300$  and  $2570\text{ cm.}^{-1}$ . By analogy with normal nitric acid, another band might be expected in the region of  $2000\text{ cm.}^{-1}$ . Because of ether bands in this region it was not possible to establish whether or not there is such an absorption band. The band at  $2570\text{ cm.}^{-1}$  appears as a shoulder on the O-D stretching band of free deuteriogenic acid, but is clearly seen in Figure 3c.

*Discussion.*—The observation in the infrared spectrum of the nitric acid-ether complexes of a strong central band accompanied by approximately equally spaced bands on the high and low frequency sides parallels observations that have now been made for several gaseous hydrogen bonded complexes and reported in earlier Parts of this Series of Papers.

The strong central band in the present case may be assigned as the O-H stretching frequency for the complex, having a displacement from the free O-H stretching frequency of about  $450\text{ cm}^{-1}$ , the exact value depending on the ether as shown in Table 2. The assignment of the remaining two bands presents certain problems. The possibility that they arise through Fermi resonance intensification of combination bands need be considered only briefly. It has already been shown conclusively for complexes of hydrogen halides and ethers<sup>4,5</sup> that the side bands which occur there cannot have their origin in Fermi resonance with vibrational levels of the ether part of the complex. In the present case, where the proton donor is a polyatomic molecule there is the additional possibility of resonance with the levels of this part of the complex. There are, in fact, combination bands in the spectrum of nitric acid at about  $2920$  and  $3000\text{ cm}^{-1}$ . Conceivably resonance intensification and displacement of these bands might explain the band in the spectrum of the complex at  $2770\text{ cm}^{-1}$ . Alternatively it might be supposed that a band around  $2700$ — $2800\text{ cm}^{-1}$  arising from the ether part of the complex is involved in Fermi resonance. However, no such explanation can be advanced for the origin of the band at  $3470\text{ cm}^{-1}$ , for there are no bands, arising from either nitric acid or ether in this region. It is clear that Fermi resonance cannot provide an explanation of one of the two side bands. This conclusion has to be taken with the observation for several hydrogen bonded complexes of a qualitatively similar structure in which there is a central band and two side bands. An explanation of such a general observation based on accidental degeneracy is unsatisfactory. In any case for the hydrogen chloride ether complex it has been shown conclusively that neither side band has its origin in Fermi resonance.<sup>4</sup> When the observations on nitric acid in either complex are taken in conjunction with the more general information it seems that in this case too, the main explanation of the structure is to be found outside Fermi resonance.

We examine next the suggestion that hydrogen stretching bands of hydrogen-bonded complexes may be accompanied by sum-and-difference bands.<sup>6</sup> For condensed phases the exceptional breadth of infrared bands of hydrogen bonded materials can be attributed to the blurring out of such sum-and-difference band structure,<sup>2</sup> making it difficult to test the validity of the explanation in terms of sum-and-difference bands. The study of gaseous systems where intermolecular contributions to broadening are absent is especially advantageous in this connection. For the nitric acid ether complex the two side bands are approximately equally spaced about the central O-H stretching frequency; one is  $340\text{ cm}^{-1}$  above and the other about  $365\text{ cm}^{-1}$  below. Following the interpretation that has been suggested for other complexes,<sup>1,3,4</sup> we might suppose this indicates a hydrogen bond stretching frequency of about  $350\text{ cm}^{-1}$  and consequently a stretching force constant of about  $1.8\text{ md}/\text{\AA}$ . This would indicate a much stronger hydrogen bond than for any other of the complexes reported in earlier Parts of this Series of Papers. The highest value previously obtained is for hydrogen fluoride-ether complexes, where  $k$  is approximately  $0.5\text{ md}/\text{\AA}$ . In this connection, it is of interest to note that the equilibrium constant for the formation of the complex is also larger than those for other complexes so far examined. This lends some support to the idea of a greater force constant for nitric acid-ether complexes than for the others, but even so the force constant is unexpectedly high compared with that for the hydrogen fluoride complex. At the same time this assignment is not easily reconciled with the spectrum of the complex formed by deuteronic acid and dimethyl ether. The band observed in this spectrum at  $2300\text{ cm}^{-1}$  clearly arises from the O-D stretching vibration. The isotopic substitution ratio of 1:36 is closely similar to

<sup>4</sup> J. E. Bertie and D. J. Millen, *J.*, 1965, 497.

<sup>5</sup> J. Arnold and D. J. Millen, *J.*, 1965, 503.

<sup>6</sup> M. I. Batuev, *Zhur. fiz. Khim.*, 1949, **23**, 1399, and *Izvest. Akad. Nauk ser. Fiz.*, 1950, **14**, 429; B. I. Stepanov, *Zhur. fiz. Khim.*, 1945, **19**, 507 and 1946, **20**, 408, *Nature*, 1946, **157**, 508; M. V. Wolkenstein, M. A. Eliashevich, and B. I. Stepanov, *Zhur. fiz. Khim.*, 1950, **24**, 1158; N. Sheppard, "Hydrogen Bonding," ed. D. Hadzi, Pergamon Press, 1959.

those for other complexes. If the band at  $2570\text{ cm.}^{-1}$  is taken to be a sum band, then a fundamental of about  $270\text{ cm.}^{-1}$  is indicated, whereas the corresponding frequency for the complex of normal isotopic nitric acid is  $340\text{ cm.}^{-1}$ . This large isotopic shift is difficult to reconcile with the assumption that the fundamental mode concerned is the stretching of the hydrogen bond. A change of this magnitude on deuteration would normally be taken as implying that a hydrogen motion was involved. The only vibration which could conceivably be involved here is the O-H torsional mode. But this has a frequency of  $465\text{ cm.}^{-1}$  for free nitric acid ( $365\text{ cm.}^{-1}$  for  $\text{DNO}_3$ ) and it would probably be expected that on formation of a hydrogen bonded complex the torsional frequency would increase. There is insufficient evidence at the present time to settle this assignment with confidence.

#### EXPERIMENTAL

All spectra were recorded on a Unicam S.P. 100 infrared spectrometer using cells of 10 cm. path length, fitted with silver chloride windows. The experimental techniques have been described previously. The ethers were obtained and purified as before, and deuterio nitric acid was distilled from a solution of potassium nitrate in deuteriosulphuric acid.

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